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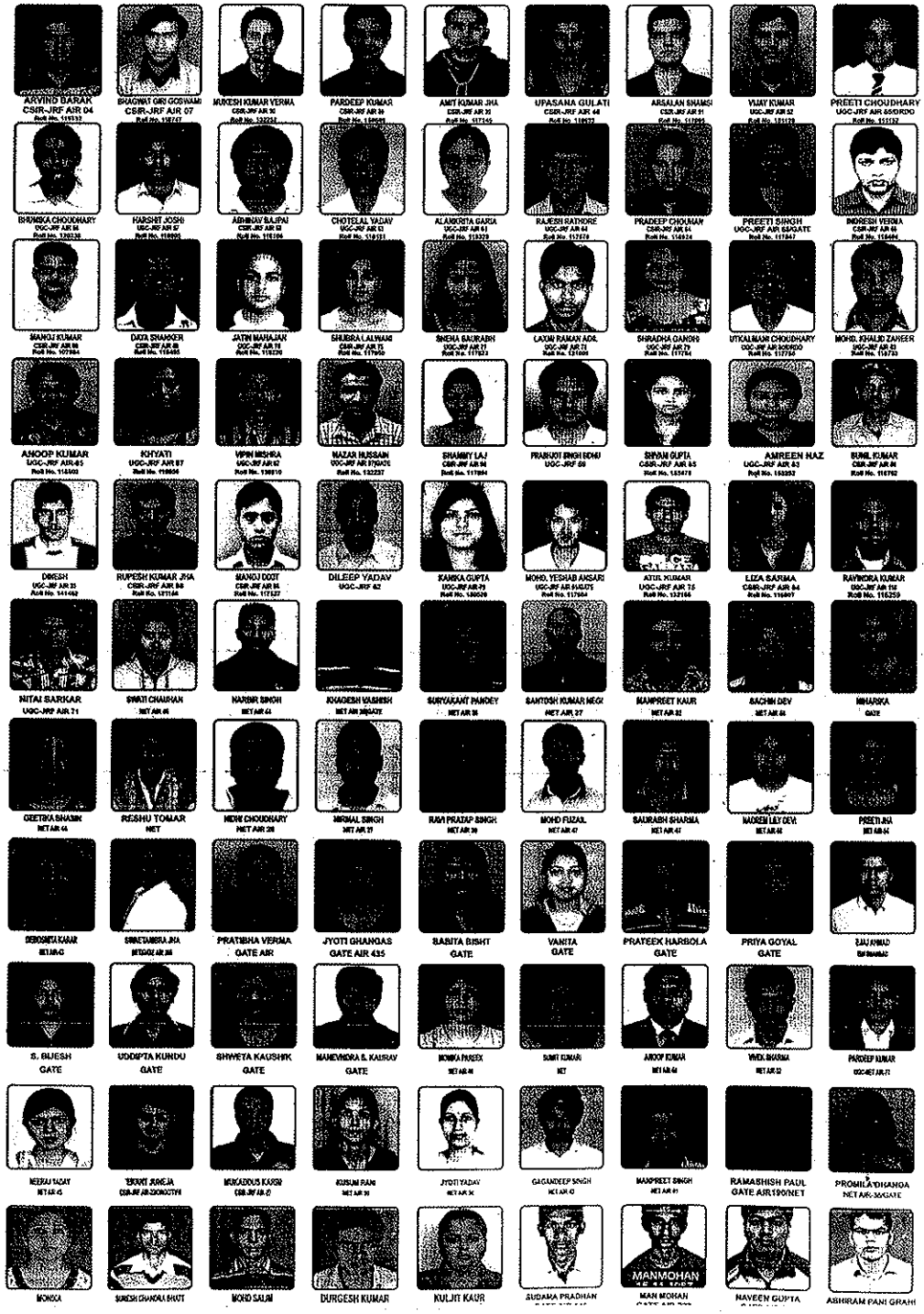

Atomic Structure & Chemical Bonding

for

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Atomic Structure

(I) Atomic Spectra of Hydrogen Atom and the Bohr's Theory

(a) $c = \nu\lambda$

where, c = velocity of light (mtr/sec) or cm/sec
λ = wavelength of light (mtr) or cm
ν = frequency of light (cycle/sec) or Hz

(b) $\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$ Lyman series (UV region)

$n = 2, 3, 4, 5, \ldots\ldots\ldots$

$= R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$ Balmer series (UV-visible region)

$n = 3, 4, 5, \ldots\ldots\ldots$

$= R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$ Paschen series (IR region)

$n = 4, 5, 6, \ldots\ldots\ldots$

$= R\left(\frac{1}{4^2} - \frac{1}{n^2}\right)$ Bracket series (IR region)

$n = 5, 6, 7, \ldots\ldots\ldots$

$= R\left(\frac{1}{5^2} - \frac{1}{n^2}\right)$ Pfund series (IR region)

$n = 6, 7, 8, \ldots\ldots\ldots$

$= R\left(\frac{1}{6^2} - \frac{1}{n^2}\right)$ Humphrey series (IR region)

$n = 7, 8, 9, \ldots\ldots\ldots$

where, $\bar{\nu}$ = wave number
λ = wavelength
R = Rydberg constant

General equation $\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$n_2 > n_1$

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(c) $mvr = \frac{nh}{2\pi}$ = Angular momentum

h = plank constant
n = principal quantum no. = 1, 2, 3, ...
m = mass of electron
v = velocity of electron
r = radius of orbit

(d) $\Delta E = E_{n_2} - E_{n_1} = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$

E_{n_2} = Energy of higher orbit (excited state)

E_{n_1} = Energy of lower orbit (ground state)

If $n_2 > n_1$ emission spectra

If $n_2 < n_1$ absorption spectra

(e) Bohr's Atomic Radius: $r = 0.529 \times \frac{n^2}{Z}\text{ Å} = 0.529 \times 10^{-8}\frac{n^2}{Z}\text{ cm}$

n = principal quantum number

z = number of protons in nucleus

This equation is valid for only those species which have one electron only, e.g., H, He^+, Li^{2+}

For H, $z = 1$

For He^+, $z = 2$

For Li^{2+}, $z = 3$

For H-atom, $r = 0.529$ Å

(f) Energy of Electron: $E_n = -13.6 \times \frac{Z^2}{n^2}$ ev/atom

This equation is valid for only those species which have only single electron like H, He^+, Li^{2+}.

(g) Velocity of Electron in Orbit:

(for H-atom)

v_1 = velocity of electron in I orbit

or

(h) No. of lines in Hydrogen Spectrum:

Ex. 1: $n_1 =$ [illegible] $= 2$

No. of lines [illegible] $+1 = 3$

Ex. 2: $n_1 =$ [illegible]

No. of lines [illegible]

(i) No. of fine lines in hydrogen atom spectrum:

$= n_1 \times n_2$

If $n_1 = 3$, $n_2 = 4$

No. of fine lines $= 4 \times 3 = 12$

(j) Increasing Order of Energy in Orbits:

$E_1 < E_2 < E_3 < E_4$.....

$mgr_1 < mgr_2 < mgr_3 <$ .....

(2) Theory of Relativity

According to theory of relativity, the mass (m_1) of electron at high speed is given by

$$m_1 = \frac{m}{\sqrt{\left[1 - \left(\frac{u}{c}\right)^2\right]}}$$

m = mass of rest; u = velocity (normal); c = velocity of light

if $u = c$, $m_1 = \infty$

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(3) Plank's Quantum Theory

Radiant energy is emitted or absorbed only in discrete units or packets of energy called photon (quantum)

$$E = \frac{hc}{\lambda} = h\nu = hc\bar{\nu} \qquad \left(\bar{\nu} = \frac{1}{\lambda} = \text{wave number}\right)$$

$$E \propto \frac{1}{\lambda}$$

h = Plank's cott. = 6.625×10^{-34} joule sec = 6.625×10^{-27} erg sec.

c = Velocity of light = 3×10^8 m/sec = 3×10^{10} cm/sec

ν = frequency of light (sec^{-1})

$\bar{\nu}$ = wave no. of light (m^{-1} or cm^{-1})

(4) Photo Electric Effect : When light of a certain frequency (UV or x-rays) strikes on the surface of metals, electrons are ejected from the metals. This phenomenon is called photoelectric effect and the ejected electron is called photoelectron.

$M + h\nu \longrightarrow M^+ + e$

M is in its ground [illegible] or [illegible] state. The atom [illegible] ionised.

Some of the energy of photon may be used to raise the [illegible] to higher vibrational level or excited electronic level and the remaining energy is converted to K.E. of the photo electron. The kinetic energy of emitted electron is given by

$\frac{1}{2}mv^2 = h\nu - I$ or $h\nu_0$

I = Threshold energy (or the work function)

$\frac{1}{2}mv^2$ = kinetic energy of photoelectron

$\therefore$ $h\nu - h\nu_0 = h(\nu - \nu_0)$

This equation is called Einstein photoelectric equation.

$h\nu_0$ = Threshold energy

ν_0 = Threshold frequency

- For each metal a certain minimum frequency of incident light is needed to eject electrons. This is known as threshold frequency, ν_0, A light of smaller frequency than this can not eject electrons no matter how long it falls on the metal surface or how high is its intensity.
- K.E. of ejected electrons is independent of the intensity of the incidant radiation, but varies linearly with its frequency.
- The no. of ejected electrons from the metal surface depends upon the intensity of the incident radiation. Greater the intensity, the larger is the no. of electrons. No. of ejected electrons do not depend upon the frequency of incident light.
- Each photon having minimum energy equal to threshold energy ejects one electron only.

Note : Cs (Cesium) emitts electron in visible light

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(5) Dual Nature of Electron (i.e, Particle and Wave Nature of Electron)

$$\lambda = \frac{h}{mu} = \frac{h}{p} \qquad \text{(de Broglie equation)}$$

u = velocity of electron; m = mass of electron

h = plank's constant; λ = wavelength of electron; p = momentum of electron

This equation is also valid for other microparticles (like Neutron and Proton).

(6) Heisenberg Uncertainty Principle

It is impossible to determine precisely both the position and the momentum (or velocity) of small moving particle simultaneously.

Mathematically,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \times \Delta p \geq \frac{\hbar}{2}$$

or $\Delta x \times m\Delta v \geq \frac{h}{4\pi}$ $\hbar \rightarrow h$ bar

or $\Delta x \times \Delta$ $\hbar = \frac{h}{2\pi}$

where Δp = uncertainty in momentum

Δv = uncertainty in velocity

Δx = uncertainty in position

Another form of the uncertainty principle

$\Delta t \times \Delta E \geq \frac{h}{4\pi}$ or $\Delta t \times \Delta E \geq \frac{\hbar}{2}$

Operators

An operator is a mathematical operation that is applied to a function. For example : $\frac{\partial}{\partial x}$ is the operator that indicates that the function is to be differentiated with respect to x and $\hat{x}$ is the operator that indicates that the function is to be multiplied by x. The operator is designated with a caret as in $\hat{A}$ or $\hat{H}$.

Linear operator : It has the following properties

$\hat{A}(f_1 + f_2) = \hat{A}f_1 + \hat{A}f_2$

$\hat{A}(cf) = c\hat{A}f$ (c is a number)

Simplest operator is the identity operator $\hat{I}$ for which $\hat{I}f = f$

There is an algebra of linear operators and we can write

$\hat{A}_3 = \hat{A}_1 + \hat{A}_2$ or $\hat{A}_4 = \hat{A}_1\hat{A}_2$

Problem :

(i) Apply the operator $\hat{A} = \frac{d}{dx}$ to function x^2

(ii) Apply the operator $\hat{A} = \frac{d^2}{dx^2}$ to the function $4x^2$

(iii) Apply the operator $\hat{A} = \left(\frac{\partial}{\partial y}\right)_x$ to the function xy^2

(iv) Apply the operator $\hat{A} = i\hbar\, d/dx$ to the function e^{-ikx}

(v) Apply the operator $\hat{A}\hat{A} = \hat{A}^2 = (-i\hbar\, d/dx)(-i\hbar\, d/dx) = \hbar^2\, d^2/dx^2$ to the function e^{-ikx}

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Solution:

(i) $\hat{A}(x^2) = \frac{d}{dx}x^2 = 2x$

(ii) $\hat{A}(4x^2) = \frac{d^2}{dx^2}(4x^2) = \frac{d}{dx}(8x) = 8$

(iii) $\hat{A}(xy)^2 = \left\{\frac{\partial}{\partial y}(xy^2)\right\}_x = 2xy$

(iv) $\hat{A}(e^{-ikx}) = -i\hbar\frac{d}{dx}e^{-ikx} = i^2 k\hbar e^{-ikx} = -k\hbar e^{-ikx}$ $(\because i^2 = -1)$

(v) $\hat{A}^2(e^{-ikx}) = -\hbar^2\frac{d^2}{dx^2}e^{-ikx} = ik\hbar^2\frac{d}{dx}e^{-ikx} = -i^2k^2\hbar^2 e^{-ikx} = k^2\hbar^2 e^{-ikx}$

Eigen Functions and Eigen Values

The significant values of f are called eigen functions and other values corresponding to the eigen functions are called eigen values.

Normal, Orthogonal and Orthonormal Wave functions

A wave function ψ is said to be normalised if

$\int \psi^* \psi\, d\tau = 1$ ...(1)

Two wave functions ψ_i and ψ_j are said to be orthogonal if

$\int \psi_i^* \psi_j\, d\tau = 0$ ...(2)

These two relations can be combined by writing

$\int \psi_i^* \psi_j\, d\tau = \delta_{ij}$ (δ_{ij} is Kronecker delta

$\delta_{ij} = 0$ for $i \neq j$

$= 1$ for $i = j$ ...(3)

Wave functions which are both normalised and orthogonal are called orthonormal wave functions.

The wave functions which satisfy equation (3) are said to be orthonormal.

The Schrödinger Wave Equation

For a standing wave (such as a vibrating string) of wavelength λ, whose amplitude at any point along x may be described by a function $f(x)$, it can be shown that:

$$\frac{d^2 f(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2} f(x) \qquad \ldots(1)$$

If an electron is considered as a wave which moves in only one dimension then:

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \qquad \ldots(2)$$

An electron may move in three directions x, y and z so this becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\psi \qquad \ldots(3)$$

Using the symbol ∇ instead of the three partial differentials, this is shortened to

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$$\nabla^2\psi = -\frac{4\pi^2}{\lambda^2}\psi \qquad \ldots(4)$$

The de Broglie relationship states that

$$\lambda = \frac{h}{mv} \qquad \ldots(5)$$

(where h is Plack's constant, m is the mass of an electron and v its velocity); hence:

$$\nabla^2\psi = -\frac{4\pi^2 m^2 v^2}{h^2}\psi \qquad \ldots(6)$$

or

$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 \qquad \ldots(7)$$

However, the total energy of the system E is made up of the kinetic energy K plus the potential energy V

$$E = K + V \qquad \ldots(8)$$

so

$$K = E - V \qquad \ldots(9)$$

But the kinetic energy $= \frac{1}{2}mv^2$

$$\ldots(10)$$

and

$$= \frac{2}{m}(E \qquad \ldots(11)$$

Substituting for v in equation (7) gives the well-known form of the Schrodinger equation

$$\frac{8\pi^2 m}{h^2} \qquad \ldots(12)$$

Acceptable Solutions to Schrodinger Wave Equation

Acceptable solutions to the wave equation, that is solutions which are physically possible, must have certain properties:

1. ψ must be continuous.
2. ψ must be finite.
3. ψ must be single valued.
4. The probability of finding the electron over all the space from plus infinity to minus infinity must be equal to one.

   The probability of finding an electron at a point x, y, z is ψ^2, so $\int_{-\infty}^{+\infty} \psi^2 dx\, dy\, dz = 1$

5. ψ must be zero at infinity.

Several wave functions called ψ_1, ψ_2, ψ_3..... will satisfy these conditions to the wave equation, and each of these has a corresponding energy E_1, E_2, E_3.....

Physical Significances of ψ and ψ^2

ψ has only mathematically significance. It has no physical significances because it can have real as well as imaginary values. Imaginary value of ψ never explain any property of the wave.

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ψ^2 is the square of the wave function, ψ. It represents the intensity of electron wave at a particular point. In other words, the greater the value of ψ^2 at a particular point, the greater is the probability of finding the electron at that point. In order to avoid imaginary values $\psi\psi^*$ is used for ψ^2. ψ^* is a complex conjugate of ψ. $\psi\psi^* d\tau$ gives the probability of finding the electron in the volume $d\tau$. The wave function ψ may be positive, negative or imaginary but the probability density $\psi\psi^*$ will always be positive and real. The probability of finding the electron is finite, which means $\psi\psi^*$ must give real values. If ψ is imaginary value, then it can be expressed as $\psi = a + ib$

Where a and b are real numbers and $i = \sqrt{-1}$. In such a case ψ is made real by multiplying it by its own complex conjugate (ψ^*) which is expressed as

$$\psi^* = a - ib$$

$$\psi\psi^* = (a + ib)(a - ib) = a^2 - (i^2 b^2)$$

$$= a^2 - (-1 \times b^2) \qquad (\because i = \sqrt{-1})$$

$$= a^2 + b^2 \qquad (\because i^2 = -1)$$

However ψ is real then $\psi = \psi^*$ then $\psi\psi^* = \psi^2$

Hydrogen Atom: Schrodinger wave equation for a particle

$$\frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \ldots(1)$$

This equation can be solved completely for the hydrogen atom and for the ion like He^+, Li^{2+}. Schrödinger equation for hydrogen can be better written in terms of polar coordinates, r, θ and φ and such an equation can be solved by separating the variables.

$$\psi(r, \theta, \phi) = R(r)\,\theta(\theta)\,\phi(\phi)$$

where $R(r)$ = Radial wave function which depends only on r.

$\theta(\theta)$ = Angular wave functions which depends only on θ.

$\phi(\varphi)$ = Angular wave function which depends only on. φ

Each value of $R(r)$, besides depending on r, also depends on two constants n and l. $R(r)$ is, therefore generally written as $R_{n,l}$. n and l are called the principal and azimuthal quantum number respectively since they represents the quantisation of definite physical properties about the electron in the atom.

The value of radial wave function $R_{n,l}$ for 1s, 2s, 2p, 3s states are given below:

	n	l	$R_{n,l}$
For 1s	1	0	$R_{1,0} = 2\left(\frac{z}{a_0}\right)^{3/2} e^{-zr/a_0}$
For 2s	2	0	$R_{2,0} = \left(\frac{z}{2a_0}\right)^{3/2}\left(2 - \frac{zr}{a_0}\right)e^{-zr/2a_0}$
For 2p	2	1	$R_{2,1} = \frac{1}{\sqrt{3}}\left(\frac{z}{2a_0}\right)^{3/2}\left(\frac{zr}{a_0}\right)e^{-zr/2a_0}$
For 3s	3	0	$R_{3,0} = \frac{2}{3}\left(\frac{z}{3a_0}\right)^{3/2}\left(3 - \frac{2zr}{a_0} + \frac{2z^2r^2}{9a_0^2}\right)e^{-zr/3a_0}$

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where a_0 = Bohr's atomic radius = 0.529 Å and z = Atomic number

Values of $\theta(\theta)$ besides depending on the angle θ, also depend on l and m. Thus $\theta(\theta)$ is generally represented as $\theta(\theta)_{l,m}$ or simply $\theta_{l,m}$. The value of m depends on the value of l. Thus m has $(2l + 1)$ values for a given value of l. If the values of l and m are known for a given orbital, the value of $\theta_{l,m}$ for an orbital can be written as shown below:

(i) $\theta_{0,0}\ (l = 0, m = 0) = \dfrac{\sqrt{2}}{2} = \dfrac{1}{\sqrt{2}}$ (s-orbital)

(ii) $\left.\begin{aligned}\theta_{1,0}\ (l = 1, m = 0) &= \sqrt{\frac{3}{2}}\cos\theta \\ \theta_{1,\pm1}\ (l = 1, m = \pm1) &= \sqrt{\frac{3}{2}}\sin\theta\end{aligned}\right\}$ (p-orbitals)

(iii) $\theta_{2,0}\ (l = 2, m = 0) = \sqrt{\frac{5}{2}}(3\cos^2\theta - 1)$

$\theta_{2,\pm1}\ (l = 2, m = \pm1) = \sqrt{\frac{15}{4}}(\sin\theta\cos\theta)$ } d-orbitals

$\theta_{2,\pm2}\ (l = 2, m = \pm2) = \sqrt{\frac{15}{4}}\sin^2\theta$

Each value of $\phi(\varphi)$ besides depending on the angle φ, also depends upon m (magnetic quantum no.). Hence the angular wave function $\phi(\varphi)$ is also represented by $\phi(\varphi)_m$ or simply ϕ_m. m fixes the direction of the angular momentum and hence fixes the direction of the orbital in space.

If the value of m for a given orbital is known, the value of $\phi(\varphi)$ for the orbital can be written as shown below:

$\phi_0\ (m = 0) = \dfrac{1}{\sqrt{2\pi}}$

$\phi_{+1}(m = +1) = \dfrac{1}{\sqrt{2\pi}}e^{i\varphi} = \dfrac{1}{\sqrt{2\pi}}(\cos\varphi + i\sin\varphi)$

$\phi_{-1}(m = -1) = \dfrac{1}{\sqrt{2\pi}}e^{-i\varphi} = \dfrac{1}{\sqrt{2\pi}}(\cos\varphi - i\sin\varphi)$,

$\phi_{+2}(m = +2) = \dfrac{1}{\sqrt{2\pi}}e^{+2i\varphi} = \dfrac{1}{\sqrt{2\pi}}(\cos 2\varphi + i\sin 2\varphi)$

$\phi_{-2}(m = -2) = \dfrac{1}{\sqrt{2\pi}}e^{-2i\varphi} = \dfrac{1}{\sqrt{2\pi}}(\cos 2\varphi - i\sin 2\phi)$

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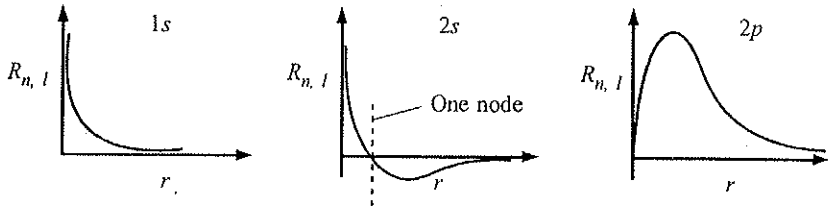
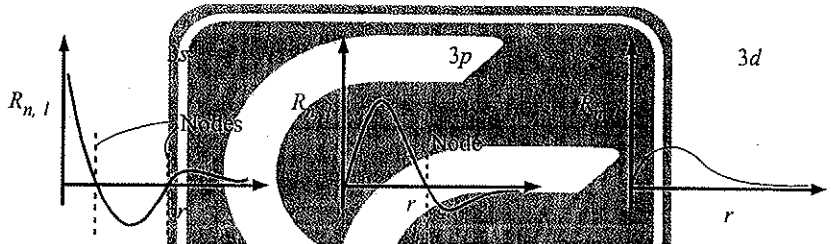
Plot of $R_{n,l}$ against r

The plot of $R_{n,l}$ versus r for the electron present in 1s, 2s, 2p, 3s, 3p and 3d are shown below:





The locations where the radial wave function passes through zero are called radial nodes. All orbitals approaches zero exponentially at large distances from the nucleus, but as they do not pass through zero at infinity, the zeros are not nodes.

The zero at the nucleus is not a radial node because the radial wave function does not pass through zero. The wave function does pass through it is poised to pass through zero at $r = 0$, however only non negative radius values are significant.

A 1s ($n = 1$, $l = 0$, $z = 1$), the wave functions $R_{n,l}$ decays exponentially with distance from the nucleus and never passes through zero. All orbitals decay exponentially at sufficient great distances from the nucleus, but some orbitals oscillate through zero close to nucleus and thus have one or more radial nodes before begining their final exponential decay.

Number of radial nodes or nodal points = $n - l - 1$ (independent of m)

For 2s orbital, $R_{2,0}$ may be zero or positive or negative.

$R_{2,0}$ = Positive, when $\dfrac{zr}{a_0} < 2$; $R_{2,0}$ = Negative, when $\dfrac{zr}{a_0} > 2$; $R_{2,0} = 0$, when $\dfrac{zr}{a_0} = 2$

Number of radial node or nodal point for 2s orbital = $n - l - 1 = 2 - 0 - 1 = 1$

For 3s orbital, no. of radial nodes = $3 - 0 - 1 = 2$

For 2p orbital, no of radial nodes = $2 - 1 - 1 = 0$

Note : Number of angular nodes = l

These graphs $R_{n,l}$ versus r have no physical significances because of the following facts:

1. The value of $R_{n,l}$ for 1s, 2s, 3s ..... is maximum at $r = 0$, i.e., the probability of finding the electron at the nucleus is maximum. This conclusion can not be true, since the actual

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probability of finding the electron at the nucleus is zero. Thus $R_{n,l}$ cannot be related with the probability of finding electron.

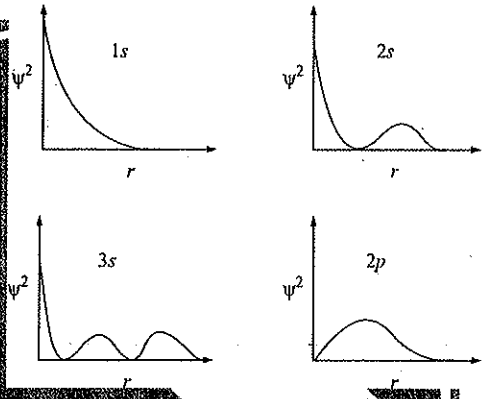
2. $R_{n,l}$ has both positive as well as negative values as evident from the above curves for $2s$ and $3s$ orbitals. The negative values of probability density cannot be possible.

Note : For $n = 2$, the decay is slower than that for $n = 1$

To overcome the above problems we plot the graphs $R^2_{n,l}$ versus r.

Plots of $R^2_{n,l}$ versus r :

The plots of $R^2_{n,l}$ versus r for the electron present in $1s$, $2s$, $3s$, $2p$ orbitals are shown below:



Because we are principally interested in the probability of finding electrons at various points in space, we shall be more concentrated with the squares of the radial wave function ($R^2_{n,l}$) than the radial wave functions themselves. It is the square of the wave function that provides the electron density or probability of finding an electron at a point in space. In these plots, values of $R^2_{n,l}$ are positive. It is important to note that for s orbitals the maximum electron density is at the nucleus, all other orbitals have zero electron density at the nucleus. The maximum value of $R^2_{n,l}$ for s orbitals at nucleus is not possible. Thus although the values of $R^2_{n,l}$ are positive. $R^2_{n,l}$, like $R_{n,l}$ can not related with the probability density of the electron. The above discussion shows that neither $R_{n,l}$ nor $R^2_{n,l}$ can be directly related with the probability density of finding an electron at a point distant r from the nucleus. Thus we draw the plots of **Radial Distribution Function** or Radial probability distribution versus r.

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Radial Distribution Function or Radial Probability Distribution or Probability of Finding Electron

The probability of finding an electron in space round the nucleus is called Radial Probability function (F_R). The value of F_R for an spherical shell of radius r and thickness dr round the nucleus is given by

F_R = (volume of spherical shell) (probability density)

$$= \left[\frac{4\pi}{3}(r+dr)^3 - \frac{4}{3}\pi r^3\right] \times R^2_{n,l}$$

$$= \frac{4}{3}\pi[r^3 + dr^3 + 3r^2dr + 3rdr^2 - r^3] \times R^2_{n,l}$$

$$= \frac{4}{3}\pi[dr^3 + 3r^2dr + 3rdr^2] \times R^2_{n,l}$$

Since dr^3 and dr^2 are very small, so these can be neglected.

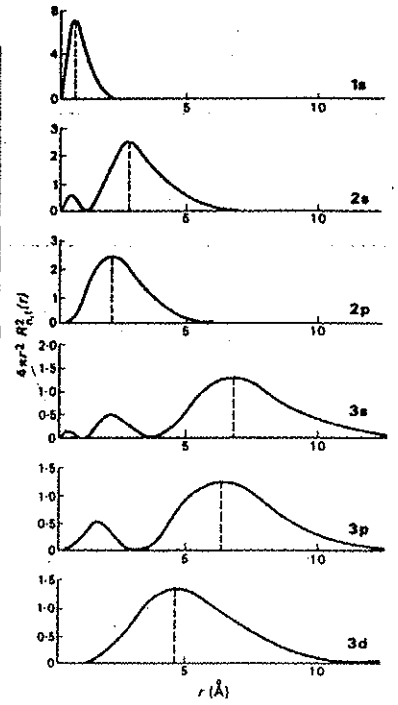
Thus $F_R = \frac{4}{3}\pi \times 3r^2dr \times R^2_{n,l}$ or $F_R = 4\pi r^2 R^2_{n,l}\, dr$

Plot the Radial Probability funtion (F_R) versus r

The raidal probability function within the shell of thickness dr is equal to $4\pi r^2 R^2_{n,l}\, dr$.

Radial distribution function between $r = 0$ and $r = r$ is equal to $\int_{r=0}^{r=r} 4\pi r^2 R^2_{n,l}\, dr$

When a graph is plotted for radial probability function versus r, such graph is called as radial probability distribution curve or simply radial distribution curve. These curves for $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$ are shown below:



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These diagrams show that the probability of finding electron is zero at the nucleus (as $r = 0$) and by examining the plots for 1*s*, 2*s* and 3*s* that the most probable distance increases as the principal quantum number increases. Furthermore, by comparing 2*s* and 2*p* or 3*s*, 3*p* and 3*d*, it can be seen that the most probable radius decreases slightly as the subsidiary quantum number increases. All the *s*-orbitals except 1*s*, have a shelll like structure, rather like an onion or a hailstone, consisting of concentric layers of electron density. Similarly all orbitals except 2*p*, 3*d* and 4*f* - orbitals have shell structure.

The number of minima appearing in a particular curve gives the no. of radial nodes or nodal points for the orbital.

Higher the no. of radial nodes, larger will be the size of orbital.

Due to the greater no. of radial nodes for 3*s*-orbital than that for 1*s* and 2*s*-orbitals, this orbital is bigger in size and more diffused than both the orbitals (1*s* and 2*s*).

Curves start from the origin and the area covered by the envelopes of a particular curve go on increasing from left to right so that the area of last envelop is maximum.

The peak of last envelop of each curve gives the distance from the nucleus where the probability of finding the electron is maximum. This distance is called as radius of maximum probability and is denoted by r_{max}.

For 1*s* orbital (for H-atom) the value of r_{max} is 0.529 Å (52.9 pm). This value is same as that calculated from Bohr's theory. In general the no. of maxima in the radial distribution plot of *s*-orbitals in equal to *n*.

Hybridisation

Hybridisation is the mixing of the atomic orbitals belonging to the same atom with slightly different energies resulting in the formation of new orbitals of equal energy and shapes. The new orbitals so formed are designated as hybrid orbitals and phenomenon is called hybridisation.

C.N.	Hybridisation	Orbitals (in valence shell)	Bond Angle (*s*)	Shape	Example
2	*sp*	*s* and p_x	180°	Linear	$[Ag(NH_3)_2]^+$
3	sp^2	*s*, p_x and p_y	120°	Triangular planar	BCl_3
4.	sp^3	*s*, p_x, p_y and p_z	109°28'	Tetrahedral	CX_4 X = H, Cl
4	sd^3	*s*, d_{xy}, d_{yz}, d_{zx}	109°28'	Tetrahedral	MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-}

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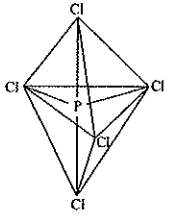
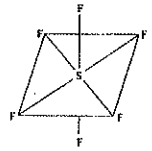
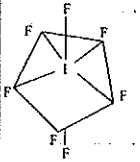
4	dsp^2 or sp^2d	$s, p_x, p_y, d_{x^2-y^2}$	90°	square planar	$[Ni(CN)_4]^{2-}$ (dsp^2)
		$s, p_x, p_y, d_{x^2-y^2}$	90°	square planar	$[Cu(NH_3)_4]^{2+}$ (sp^2d)
5	dsp^3*	s, p_x, p_y, p_z, dz^2	90°, 120°	Trigonal pyramidal	PCl_5 
5	dsp^3	p_x, p_y, p_z and $d_{x^2-y^2}$		Square pyramidal	$[Ni(CN)_5]^{3-}$
6	sp^3d^2	p_x, p_y, p_z and d_{z^2}	90°, 90°	Octahedral	SF_6 
7.	sp^3d^3		72°, 90°	Pentagonal bipyramidal	IF_7 

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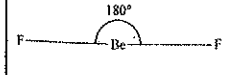
[**Note :** Lone pair of electrons reside in the hybrid orbitals, σ-bonds are formed by hybrid orbitals and π-bonds are formed by atomic orbitals of central metal atom with other atom.]

1. *sp* HYBRIDISATION

BeF_2 or $BeCl_2$

Be → (E.C.) $1s^2\ 2s^2\ 2p^0$

Valence shell configuration		2s	2p
	Be atom in ground state	↑↓	
	Be atom in excited state	↑	↑
	Be atom in molecules	↑↓	↑↓
Angle 180°	Linear Shape		*sp*-Hybridisation

NO_2^+
$N^+ \rightarrow$ (E.C.) $1s^2\ 2s^2\ 2p^2$

Valence shell configuration

$O = \overset{+}{N} = O$

Angle 180°

Note : π orbitals are ignored in determining the shape.

	2s	2p		
N^+ ion in ground state	↑↓	↑	↑	
N^+ ion in excited state	↑	↑	↑	↑
N^+ ion in NO_2^+ ion	↑↓	↑↓	↑↓	↑↓

Two-π bond

Linear Shape — *sp*-Hybridisation

CO_2
C → (E.C.) $1s^2\ 2s^2\ 2p^2$

Valence shell configuration

$O = C = O$

Angle 180°

Note : π orbitals are ignored in determining the shape.

	2s	2p		
C atom in ground state	↑↓	↑	↑	
C atom in excited state	↑	↑	↑	↑
C atom in CO_2 molecule	↑↓	↑↓	↑↓	↑↓

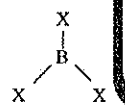
Two-π bond

Linear Shape — *sp*-Hybridisation

2. sp^2 HYBRIDISATION

BX_3
B → (E.C.) $1s^2\ 2s^2\ 2p^1$

Valence shell configuration



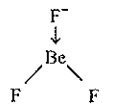
Angle 120°

	2s	2p		
B atom in ground state	↑↓	↑		
B atom in excited state	↑	↑	↑	
B atom in molecules	↑↓	↑↓	↑↓	

Trigonal Planar Shape — sp^2-Hybridisation

BeF_3^-
Be → (E.C.) $1s^2\ 2s^2$ [$F^- \rightarrow BF_3$]

Valence shell configuration



Angle 120°

Note : Coordinate bond is formed the hybrid orbitals by gaining or donating the lone pair of electrons

	2s	2p		
Be atom in ground state	↑↓			
Be atom in excited state	↑	↑		
Be atom in BeF_3^- ion	↑↓	↑↓	↑↓	

coordinate bond

Trigonal Planar Shape — sp^2-Hybridisation

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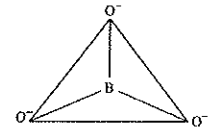
BO_3^{-3}
B → (E.C.) $1s^2\ 2s^2\ 2p^1$

Valence shell configuration



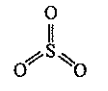
Trigonal Planar Shape

	2s	2p		
B atom in ground state	↑↓	↑		
B atom in excited state	↑	↑	↑	
B atom in BO_3^{3-} ion	↑↓	↑↓	↑↓	

sp^2-Hybridisation

SO_3
S → (E.C.) $3s^2\ 2p^4\ 3d^0$

Valence shell configuration



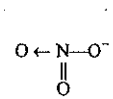
Trigonal Planar Shape

	3s	3p		3d				
S atom in ground state	↑↓	↑↓	↑	↑				
S atom in excited state	↑	↑	↑	↑	↑			
S atom in molecules	↑↓	↑↓	↑					

3 σ bonds — 1 π bond — sp^2 Hybridisation

NO_3^-
N → (E.C.) $2s^2\ 2p^3$

Valence shell configuration



	2p		
N atom in ground state	↑	↑	↑
N atom in excited state	↑	↑	↑
N atom in NO_3^- ion	↑↓	↑↓	↑↓

dative bond — σ bonds — π bond

Trigonal Planar Shape — sp^2 Hybridisation

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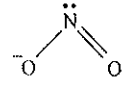
NO_2^-
N → (E.C.) $2s^2\ 2p^3$

Valence shell configuration



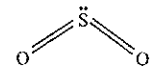
	2s	2p		
N atom in ground state	↑↓	↑	↑	↑
N atom in excited state	↑↓	↑	↑	↑
N atom in NO_2^- ion	↑↓	↑↓	↑↓	↑↓

lone pair of electron — 2 σ bonds — 1 π bond

V- Shape — sp^2-Hybridisation

SO_2
S → (E.C.) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4\ 3d^0$

Valence shell configuration



V-Shape

	3s	3p	3d
S atom in ground state	↑↓	↑↓ ↑ ↑	
S atom in excited state	↑↓	↑ ↑ ↑	↑
S atom in SO_2 molecule	↑↓	↑↓ ↑↓ ↑↓	↑↓

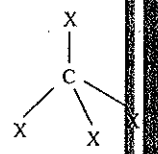
lone pair of electron — 2 σ bonds — 2 π bonds

sp^2 Hybridisation

3. sp^3 HYBRIDISATION

CX_4
C → (E.C.) $1s^2\ 2s^2\ 2p^2$
X = mono valent species = H, Cl

Valence shell configuration

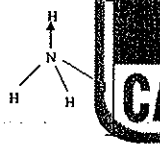


	2s	2p
C atom in ground state	↑↓	↑ ↑
C atom in excited state	↑	↑ ↑ ↑
C atom in CX_4 molecule	↑↓	↑↓ ↑↓ ↑↓

Tetrahedral Shape — sp^3-Hybridisation

NH_4^+ [$H^+ \leftarrow :NH_3$]
N → (E.C.) $1s^2\ 2s^2\ 2p^3$

Valence shell configuration

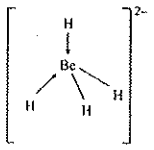


	2s	2p
N atom in ground state	↑↓	↑ ↑ ↑
N atom in excited state	↑	↑ ↑ ↑
N atom in NH_4^+ ion	↑↓	↑↓ ↑↓ ↑↓

Tetrahedral Structure — dative or coordinate bond — sp^3-Hybridisation

BeH_4^{-2} or [$H^- \rightarrow BH_2 \leftarrow H^-$]
Be → (E.C.) $1s^2\ 2s^2$

Valence shell configuration



	2s	2p
Be atom in ground state	↑↓	
Be atom in excited state	↑↓	↑
Be atom in BH_4^{2-} ion	↑↓	↑↓ ↑↓ ↑↓

Tetrahedral Structure — Two coordinate bonds — sp^3-Hybridisation

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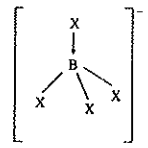
BX_4^- or [$X^- \rightarrow BX_3$]
X = Cl, Br, I, etc.
$_5B$ → (E.C.) $1s^2\ 2s^2\ 2p^1$

Valence shell configuration



Tetrahedral Structure

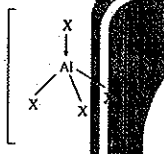
	2s	2p
B atom in ground state	↑↓	↑
B atom in excited state	↑	↑ ↑
B atom in BX_4^- ion	↑↓	↑↓ ↑↓ ↑↓

Coordinate bond

sp^3-Hybridisation

AlX_4^- or [$X^- \rightarrow AlX_3$]
X = Cl, Br, I, etc.
$_{13}Al \rightarrow$ (E.C.) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

Valence shell configuration



Tetrahedral Structure

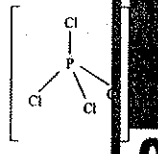
	2s	2p
Al atom in ground state	↑↓	↑
Al atom in excited state	↑	↑ ↑
Al atom in AlX_4^- molecule	↑↓	↑↓ ↑↓ ↑↓

Coordinate bond

sp^3-Hybridisation

PCl_4^+
X = H, R, etc.
$_{15}P \rightarrow$ (E.C.) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

Valence shell configuration



Tetrahedral Structure

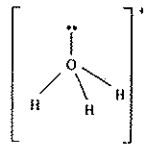
	2s	2p
P atom in ground state	↑↓	↑ ↑
P atom in excited state	↑	↑ ↑ ↑
P atom in molecules	↑↓	↑↓ ↑↓ ↑↓

Ex : SbF_4^+

sp^3-Hybridisation

H_3O^+ [$H_2O \rightarrow H^+$]
O → (E.C.) $1s^2\ 2s^2\ 2p^4$

Valence shell configuration



	2s	2p
O atom in ground state	↑↓	↑↓ ↑ ↑
O atom in excited state	↑↓	↑↓ ↑ ↑
O atom in H_3O^+ ion	↑↓	↑↓ ↑↓ ↑↓

Ex : SeF_3^+, $Te(Me)_3^+$

Pyramidal Shape or Distorted Tetrahedral — lone pair of electron — Dative bond — sp^3-Hybridisation

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	2s	2p
Valence shell ...nfiguration		
O atom in ground state	↑↓	↑↓ ↑ ↑
O atom in excited state	↑↓	↑ ↑ ↑
O atom in H_2O molecule	↑↓	↑↓ ↑↓ ↑↓
Ex.: ...SCl_2, NH_2^-	Angular or V-Shape	sp^3-Hybridisation

	5s	5p
Valence shell ...nfiguration		
I^+ in ground state	↑↓	↑↓ ↑ ↑
I^+ in excited state	↑↓	↑ ↑ ↑
...in ICl_2^- ion	↑↓	↑↓ ↑↓ ↑↓
Ex.: BrF_2^+, ClF_2^+, BrO_2^-, IF_2^-, etc.	Angular or V-Shape	sp^3-Hybridisation

	5s	5p
Valence shell ...nfiguration		
... in ground state	↑↓	↑↓ ↑ ↑
... in excited state	↑	↑ ↑ ↑
...in ICl_4^- ion	↑↓	↑↓ ↑↓ ↑↓
Ex.: BrF_4^+, ClF_4^+, BrO_4^-, IF_4^-, etc.	Square planar	sp^3d^2-Hybridisation

SO_4^{2-}

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4\ 3d^0$

Valence shell configuration	3s	3p	3d
S atom in ground state	↑↓	↑↓ ↑ ↑	
S atom in excited state	↑	↑ ↑ ↑	↑ ↑
S atom in SO_4^{2-} ion	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓

4 σ bonds — 2 π bonds

Tetrahedral Shape — sp^3 Hybridisation

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ClO_4^-
Cl → (E.C.) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5\ 3d^0$

Valence shell configuration	3s	3p	3d
Cl atom in ground state	↑↓	↑↓ ↑ ↑	
Cl atom in excited state	↑	↑ ↑ ↑	↑ ↑ ↑
Cl atom in ClO_4^- ion	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓

4 σ bonds — 3 π bonds

Tetrahedral Shape — sp^3 Hybridisation

CO_3^{-2}
C → (E.C.) $1s^2\ 2s^2\ 2p^2$

Valence shell configuration	2s	2p
C atom in ground state	↑↓	↑ ↑
C atom in excited state	↑	↑ ↑ ↑
C atom in CO_3^{-2} ion	↑↓	↑↓ ↑↓ ↑↓

1 π bond

Trigonal planar shape — sp^2-Hybridisation

4. sp^3d HYBRIDISATION

PCl_5
P → (E.C.) $3s^2\ 3p^3\ 3d^0$

Valence shell configuration	3s	3p	3d
P atom in ground state	↑↓	↑ ↑ ↑	
P atom in excited state	↑	↑ ↑ ↑	↑ ↑
P atom in PCl_5 molecule	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓

5 σ bonds

Ex. : PF_5, PCl_5, AsF_5, SbF_5, etc. — Trigonal bi pyramidal shape — sp^3d Hybridisation

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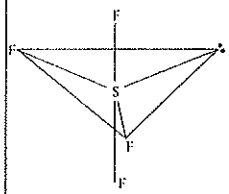
SF_4
S → (E.C.) $3s^2\ 3p^4\ 3d^0$

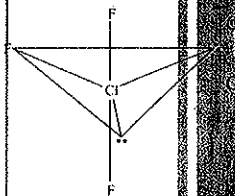


Valence shell configuration	3s	3p	3d
S atom in ground state	↑↓	↑↓ ↑ ↑	
S atom in excited state	↑↓	↑ ↑ ↑	↑
S atom in SF_4 molecule	↑↓	↑↓ ↑↓ ↑↓	↑↓

lone pair — 4 σ bonds

Distorted tetrahedral seesaw structure — sp^3d Hybridisation

ClF_3
Cl → (E.C.) $3s^2\ 3p^5\ 3d^0$

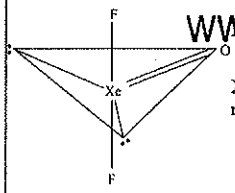


Valence shell configuration	3s	3p	3d
Cl atom in ground state	↑↓	↑↓ ↑ ↑	
Cl atom in excited state	↑↓	↑ ↑ ↑	↑ ↑
Cl atom in ClF_3 molecule	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓

lone pairs

Ex. : IF_3, $BrCl_3$, XeF_2, [illegible] etc. — [illegible] Hybridisation

$XeOF_2$
Xe → (E.C.) $5s^2\ 5p^6\ d^0$



Valence shell configuration	5s	5p	5d
Xe atom in ground state	↑↓	↑↓ ↑↓ ↑	
Xe atom in excited state	↑↓	↑ ↑ ↑	↑ ↑
Xe atom in $XeOF_2$ molecule	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓

lone pairs — 1 π bond

T-Shape — sp^3d Hybridisation

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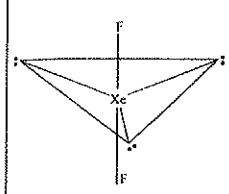
XeF_2
Xe → (E.C.) $5s^2\ 5p^6\ d^0$



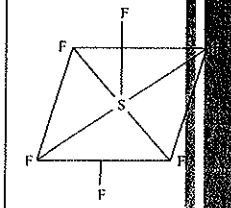
Valence shell configuration	5s	5p	5d
Xe atom in ground state	↑↓	↑↓ ↑↓ ↑↓	
Xe atom in excited state	↑↓	↑↓ ↑↓ ↑	↑
Xe atom in XeF_2 molecule	↑↓	↑↓ ↑↓ ↑↓	↑↓

lone pairs

Linear Shape — sp^3d Hybridisation

5. sp^3d^2, HYBRIDISATION

SF_6
S → (E.C.) $3s^2\ 3p^4\ 3d^0$

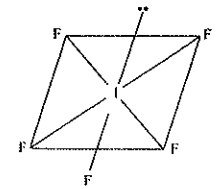


Valence shell configuration	3s	3p	3d
S atom in ground state	↑↓	↑↓ ↑ ↑	
S atom in excited state	↑↓	↑ ↑ ↑	↑ ↑
S atom in SF_6 molecule	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓

Ex.:
FeF_6^{-4}, SeF_6, $[AlF_6]^{-3}$
$[GaCl_6]^{-3}$, $[InCl_6]^{-3}$
$[SnCl_6]^{-2}$, $[PF_6]^-$, [illegible]
$[BiCl_6]^-$, $[IF_6]^+$, etc.

Octahedral Shape — sp^3d^2 Hybridisation

IF_5
I → (E.C.) $5s^2\ 5p^5\ 5d^0$



Valence shell configuration	5s	5p	5d
I atom in ground state	↑↓	↑↓ ↑↓ ↑	
I atom in excited state	↑↓	↑ ↑ ↑	↑ ↑
I atom in IF_5 molecule	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓

lone pair

Ex.: SbF_5^{-2}, XeF_5^+, $TeCl_5^-$, etc.

Distorted octahedron or square pyramidal — sp^3d^2 Hybridisation

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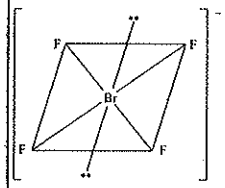
$[BrF_4^-]$ or $[F \rightarrow BrF_3]^-$

Br→ (E.C.) $4s^2\ 4p^5\ 4d^0$

Valence shell configuration	4s	4p	4d
Br atom in ground state	↑↓	↑↓ ↑↓ ↑	
Br atom in excited state	↑↓	↑↓ ↑ ↑	↑
Br atom in BrF_4^- ion	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓



lone pairs — Coordinate bond

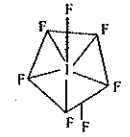
Ex.: XeF_4, IF_4^-, I_5^-, ICl_4^-, etc. **Square planar** sp^3d^2 Hybridisation

6. sp^3d^3 HYBRIDIZATION

IF_7

I → (E.C.) $5s^2\ 5p^5\ 5d^0$

Valence shell configuration	5s	5p	5d
I atom in ground state	↑↓	↑↓ ↑↓ ↑	
I atom in excited state	↑	↑ ↑ ↑	↑ ↑ ↑ ↑ ↑
I atom in IF_7 molecule	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ↑ ↑ ↑

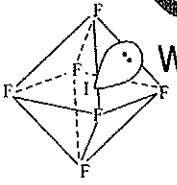


Ex.: ReF_7 etc. Pentagonal bipyramidal structure sp^3d^3 Hybridisation

AB_6 (1p) Type IF_6^- or $[F \rightarrow IF_5]$

I → (E.C.) $5s^2\ 5p^5\ 5d^0$

Valence shell configuration	5s	5p	5d
I atom in ground state	↑↓	↑↓ ↑↓ ↑	
I atom in excited state	↑↓	↑ ↑ ↑ ↑	↑ ↑
I atom in IF_6^- ion	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓



Coordinate Bond

Ex.: XeF_6, $FeCl_6^{-2}$, FeF_6^{-2}, SbX_6^{-3}, etc. **Distorted octahedral** sp^3d^2 Hybridisation

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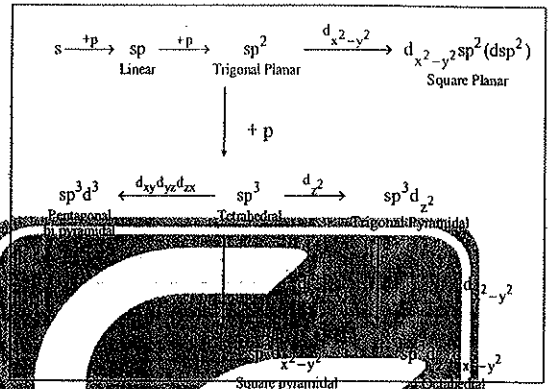
SUMMARY

In Hybridization, positive and negative charge of a molecule, we take on central atom or surrounding atom(s), depends upon the electro-negatitivity difference between two, which is more electro-negativity carry negative charge and vice-versa.

(Ex.: NH_4^+, H carries positive charge, IF_6^-, F carries negative charge.



Note : This is valid only when there is distorting / active lone pair is absent.

Valence Shell Electron Pair Repulsion Theory

A lone pair of electrons takes up more space around the central atom than a bond pair, since the lone pair attracted to one nucleus whilst bond pair is shared by two nuclei. It follows that repulsion between two lone pairs is greater than repulsion between a lone pair and a bond pair, which in turn is greater than the repulsion between two bond pairs. Thus the presence of lone pairs on the central atom causes slight distortion of the bond angles from the ideal shape. If the angle between a lone pair, the central atom and a bond pair is θ°, it follows that the actual bond angles between the atoms around the central

lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

(i) CH_4

Molecule	CH_4	Valence shell electron(s)/ No. of electron(s) participating in bonding	* *bp = bond pair, lp = lone pair*
Central Atom	C	4	
	H	4	
No. of bp & lp		4bp	
Geometry		Tetrahedron	
Shape		Regular tetrahedron	
Bond Angle		109° 28'	

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(ii) NH_3

Molecule	NH_3	Valence shell electron(s)/ No. of electron(s) participating in bonding	* *bp = bond pair, lp = lone pair*
Central Atom	N	5	
	H	3	
No. of bp & lp		3bp + 1 lp	
Geometry		Tetrahedron	
Shape		Distorted tetrahedron or pyramidal	
Bond Angle		107° 48'	

(iii) H_2O

Molecule	H_2O	Valence shell electron(s)/ No. of electron(s) participating in bonding	* *bp = bond pair, lp = lone pair*
Central Atom	O	6	
	H	2	
No. of bp & lp		2 bp + 2 lp	
Geometry		Tetrahedron	
Shape		Distorted tetrahedron or V shape	
Bond Angle		104° 27'	

(iv) BrF_5

Molecule	BrF_5	Valence shell electron(s)/ No. of electron(s) participating in bonding	* *bp = bond pair, lp = lone pair*
Central Atom	Br	7	
	F	5	
No. of bp & lp		5 bp + 1 lp	
Geometry		Octahedron	
Shape		Distorted octahedron or square pyramidal	
Bond Angle		84° 30'	

* *bp = bond pair, lp = lone pair, ep = electron pair.*

Note : (1) *Xe atom is 8 electron deficient but not electron deficient due to charge.*

(2) *pi bond does not effect the structure they only change bond length so we don't consider in VSEPR theory.*

The magnitude of repulsion between bonding pairs of electrons depends on the electrnegativity difference between the central atom and other atoms.

Double bond causes more repulsion than single bonds and triple bonds cause more repulsion than a double bond.

Double bond and triple bond causes more repulsion than single bonds–but does not effect the structure. Bond angles involving multiple bonds generally larger than those involving only single bond.

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Effect of Lone Pairs

Molecules with four electron pairs in their outer shell are based on a tetrahedron. In CH_4 there are four bonding pairs of electrons in the outer shell of the C atom, and the structure is a regular tetrahedron with bond angles H—C—H of 109°28'. In NH_3 the N atom has four electron pairs in the outer shell, made up of three bond pairs and one lone pair. because of the lone pair, the bond angle H—N—H is reduced from the theoretical tetrahedral angle of 109°28' to 107°48'. In H_2O the O atom has four electron pairs in the outer shell. The shape of the H_2O molecule is based on a tetrahedron with two corners occupied by bond pairs and the other two corners occupied by lone pairs. The presence of two lone pairs reduces the bond angle further to 104°27'.

In a similar way SF_6 has six bond pairs in the outer shell and is a regular octahedron with bond angles of exactly 90°. In BrF_5 the Br also has six outer pairs of electrons, made up of five bond pairs and one lone pair. The lone pair reduces the bond angles to 84°30'. Whilst it might be expected that two lone pairs would distort the bond angles in an octahedron still further, in XeF_4 the angles are 90°. This is because the lone pairs are trans to each other in the octahedron, and hence the atoms have a regular square planar arrangement.

Molecules with five pairs of electrons are all based on a trigonal bipyramid. Lone pairs distort the structures as before. The lone pairs always occupy the equatorial positions (in the triangle), rather than the apical positions (up and down a line from the centre). Thus the central I atom has five electron pairs in the outer shell, made up of two bond pairs and three lone pairs. The lone pairs occupy all three equatorial positions and the two atoms occupy the top, middle and bottom positions in the trigonal bipyramid, thus giving a linear arrangement with a bond angle of exactly 180°.

Effect of Electronegativity

NF_3 and NH_3 both have structures based on a tetrahedron with one corner occupied by a lone pair. The high electronegativity of F pulls the bonding electrons further away from N than in NH_3. Thus repulsion between bond pairs is less in NF_3 than in NH_3. Hence, the lone pair in NF_3 causes a greater distortion from a tetrahedral and have a F—N—F bond angle of 102°30', compared with 107°48' in NH_3. The same effect is found in H_2O (bond angle 104°27') and H_2S (bond angle 102°), H_2O (bond angle 104°27') and H_2Se (bond angle 92°2').

Isoelectronic Principle

Isoelectronic species usually have the same structure. This may be extended to species with the same number of valence electrons. Thus BF_4^-, CH_4, and NH_4^+ are all tetrahedral, CO_3^{2-}, NO_3^- and SO_3 are all planar triangles, and CO_2, N_3^- and NO_2^+ are all linear.

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EXAMPLES:

1. BF_3

Molecule	BF_3	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	B	3
	F	3
No. of bp & lp		3 bp
Geometry		Planar Triangle
Shape		Regular planar triangle
Bond Angle		120°

** bp = bond pair, lp = lone pair, ep = electron pair.*

Note : (1) Xe contain 8 electrons in valence shell and four electrons get due to charge.

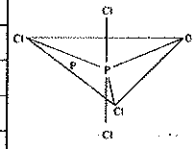
(2) pi bond does not effect the structure they only change bond length so we don consider in VSEPR theory.

2. BF_4^- ($F^- \rightarrow BF_3$)

Molecule	BF_4^-	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	B	3
	F	5 (3 from 3F atoms and 2 from F^-)
No. of bp & lp		4 bp
Geometry		Tetrahedral
Shape		Regular tetrahedral
Bond Angle		109° 28'

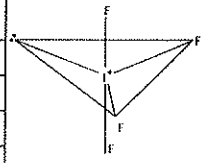
3. PCl_5

Molecule	PCl_5	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	P	5
	Cl	5
No. of bp & lp		5 bp
Geometry		Trigonal bi pyramid
Shape		Trigonal bipyramid
Bond Angle		90° and 120°
It is a completely regular structure. Symmetrical structure are more stable than asymmetric ones.		$2\,PCl_4 \rightarrow PCl_3^+ + PCl_5^-$ (Tetrahedral) (Octahedral)



4. IF_4^+

Molecule	IF_4^+	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	I	6
	F	4
No. of bp & lp		4 bp + 1 lp = 5ep
Geometry		Trigonal bi pyramid
Shape		Distorted tetrahedral or seesaw structure
Bond Angle		-----



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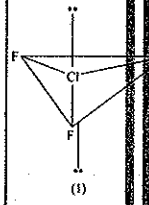
5. ClF_3

Molecule	ClF_3	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Cl	7
	F	3
No. of bp & lp		3 bp + 2 lp
Geometry		Trigonal bi pyramid
Shape		T-shape
Bond Angle		90° and 120°



(I)

- Since, in ClF_3 the Cl atom has five elecron pairs in the outer shell, hence the structure is a trigonal bipyramidal. Trigonal bipyramid is not a regular shape, since bond angle are not all the same. It therefore follows that the corners are not equivalent. Most stable structure has lowest energy, i.e., minimum repulsion between five orbitals. The greatest repulsion occurs between two lone pairs. Lone pair-bond pair repulsions are less stronger, and bond pair-bond pair repulsion the weakest. Groups at 90° to each other repel each other strongly, whilst group 120° apart repel each other much less.
  - Structure 1 most symmetrical has six 90° repulsion between lone pairs and atoms.
  - Structure 2 has One 90° repulsion between two lone pairs + Three 90° repulsion between tone pairs and atoms
  - Structure 3 has Four 90° repulsion between lone pairs and atoms. These factors indicate that structures is most probable.
- General Rule : If lone pairs occur in a trigonal bipyramid they will be located in the equatorial positions (round the middle) rather than the apical positions (top and bottom), since this arrangement minimises repulsive forces.

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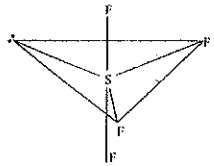
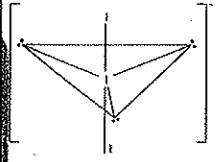
6. SF_4

Molecule	SF_4	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	S	6
	F	4
No. of bp & lp		4 bp + 1lp
Geometry		Trigonal bi pyramid
Shape		Distorted tetrahedral or seesaw structure
Bond Angle		-------



7. I_3^- $[I—I \leftarrow I]^-$ (IBr_2^- / ICl_2^- / BrF_2^-)

Molecule	I_3^-	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	I	7
	I and I^-	1+1+2=4
No. of bp & lp		3bp + 2lp = 5ep (Donate by I^-)
Geometry		Trigonal bi pyramid
Shape		Linear
Bond Angle		180°



8. SF_6

Molecule	SF_6	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	S	6
	F	6
No. of bp & lp		6bp
Geometry		Octahedral
Shape		Regular octahedral
Bond Angle		90°

9. IF_7

Molecule	IF_7	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	I	7
	F	7
No. of bp & lp		7 bp
Geometry		Pentagonal bi pyramid
Shape		Pentagonal bi pyramid
Bond Angle		72° and 90°

10. IF_5

Molecule	IF_5	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	I	7
	F	5

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No. of bp & lp		5 bp + 1lp
Geometry		Octahedral
Shape		Square based pyramid
Bond Angle		-----

11. ICl_4^- $\left[Cl^- \rightarrow ICl_3\right]$, BrF_4^-, I_5^- ($I\,I_4^-$)

Molecule	ICl_4^-	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	I	7
	3 Cl and 1 Cl^-	3 + 2 = 5
No. of bp & lp		3bp + 2lp + 1bp (donate by Cl^-) = 6 ep
Geometry		Octahedral
Shape		Square planar (Regular)
Bond Angle		90°

12. ICl_2^+ $[Cl—I—C$ $F_2^+]$, ClF_4^+

Molecule	ICl_2^+	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	I	7
	Cl	7
No. of bp & lp		2bp + 2lp = 4ep
Geometry		Tetrahedral
Shape		Angular or V shape
Bond Angle		90°

13. XeF_2

Molecule	XeF_2	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Xe	8
	F	2
No. of bp & lp		2bp + 3lp = 5ep
Geometry		Trigonal bi pyramid
Shape		Linear
Bond Angle		180°

14. XeF_4

Molecule	XeF_4	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Xe	8
	F	4
No. of bp & lp		4bp + 2lp = 6ep
Geometry		Octahedral
Shape		Square planar
Bond Angle		90°

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15. XeF_6

Molecule	XeF_6	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Xe	8
	F	6
No. of bp & lp		6 bp + 1 lp = 7 ep
Geometry		Pentagonal bi pyramid
Shape		Capped octahedron or distorted octahedron
Bond Angle		-----

16. XeO_3

Molecule	XeO_3	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Xe	8
	O	6
No. of bp & lp		3 bp (σ bond) + 3bp (π bond) + 1 lp = 4 ep (Note : σ-bond pairs and lone pairs are counted only)
Geometry		Tetrahedral
Shape		Distorted Tetrahedral or Trigonal Pyramidal
Bond Angle		109° 28'

17. XeO_2F_2

Molecule	XeO_2F_2	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Xe	8
	O	4
	F	2
No. of bp & lp		4bp (σ bond) + 2bp (π bond) + 1 lp = 5 ep (Note : σ-bond pairs and lone pairs are counted only)
Geometry		Octahedral
Shape		Distorted Tetrahedral
Bond Angle		-----

18. $XeOF_4$

Molecule	$XeOF_4$	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Xe	8
	O	2
	F	4
No. of bp & lp		5 bp (σ bond) + 1bp (π bond) + 1 lp = 6 ep (Note : σ-bond pairs and lone pairs are counted only)
Geometry		Octahedral
Shape		Square pyramidal
Bond Angle		-----

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19. XeO_4

Molecule	XeO_4	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Xe	8
	O	8
No. of bp & lp		4 bp (σ bond) + 4bp (π bond) = 4 ep (Note : σ-bond pairs and lone pairs are counted only)
Geometry		Tetrahedral
Shape		Tetrahedral
Bond Angle		109° 28'

20. XeO_3F_2

Molecule	XeO_3F_2	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Xe	8
	O	6
	F	2
No. of bp & lp		5 bp (σ bond) + 0bp (π bond) = 5 ep (Note : only σ-bond pairs electrons are counted)
Geometry		Trigonal bipyramid
Shape		Trigonal bi pyramid
Bond Angle		120° and 90°

21. $[XeO_6]^{-4}$ or Ba_2XeO_6

Molecule	$[XeO_6]^{-4}$	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Xe	8
	Six O^{-}	8 (4 + 4)
No. of bp & lp		6bp (σ bond) + 2bp (π bond) = 6 ep (Note : Only σ-bond pairs electrons are counted)
Geometry		Octahedral
Shape		Regular octahedral
Bond Angle		90°

22. $BrOF_4^-$

Molecule	$BrOF_4^-$	Valence shell electron(s)/ No. of electron(s) participating in bonding
Central Atom	Br	7
	O	2
	Three F and one F^-	5 (3 + 2)
No. of bp & lp		5 bp (σ bond) + 1bp (π bond) + 1 lp = 6 ep
Geometry		Octahedral
Shape		Square pyramid
Bond Angle		

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MOLECULAR ORBITAL THEORY

The salient features of this theory are:

(i) Just as electrons of atoms are present in various atomic orbitals, electrons of a molecule are present in various molecular orbitals.

(ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmery.

(iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus an atomic orbital is monocentric while a molecular orbital is polycentric.

(iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called bonding molecular orbital and antibonding molecular orbital are formed.

(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.

(vii) The molecular orbitals like atomic orbitals are filled in accordance with the **Aufbau** principle obeying the Pauli exclusion principle and Hund's rule.

Formation of Molecular Orbitals: Linear Combination of Atomic Orbitals (LCAO)

Molecular orbitals which are one-electron wave functions for molecules are difficult to obtain directly from the solution of the Schrodinger equation. This difficulty is overcome by resorting to an approximate method called the linear combination of atomic orbitals (LCAO) method to form molecular orbitals.

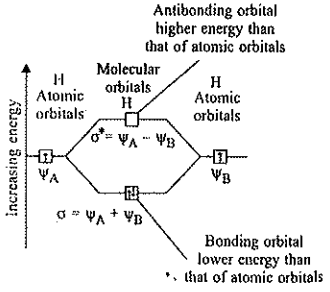
Let us consider the application of the LCAO method to the homonuclear diatomic hydrogen molecule. The two hydrogen atoms in the H_2 molecule for the sake of convenience may be labelled as A and B. Each hydrogen atom in ground state has an electron in the 1s orbital. These atomic orbitals may be represented by the wave functions ψ_A and ψ_B. Mathematically the formation of molecular orbitals is described by the linear combination (addition or subtraction) of the wave functions of the individual atomic orbitals, *i.e.*,

$$\psi_{MO} = \psi_A \pm \psi_B$$

Therefore, two molecular orbitals σ and σ^* are formed $\sigma = \psi_A + \psi_B$ & $\sigma^* = \psi_A - \psi_B$

The molecular orbital σ formed by the addition of atomic orbitals is called the bonding molecular orbital and the molecular orbital σ^* formed by the subtraction of atomic orbitals is called antibonding molecular orbital.

Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other (constructive interference) while in the formation of antibonding molecular orbital, these electron waves cancel each other (destructive interference). The result is that in a bonding molecular orbital most of the electron density is located between the nuclei of the bonded atoms and hence the repulsion between the nuclei is very low while in an antibonding molecular orbital, most of



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the electron density is located away from the space between the nuclei, as a matter of fact there is a nodal plane (i.e., plane on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. A bonding molecular orbital is, therefore, always of lower energy than either of the atomic orbitals that have combined to form it. In contrast, electrons placed in the antibonding molecular orbital destabilizes the molecule. The attraction between the electrons and the nuclei is less than the mutual repulsion of electrons in this orbital and this produces a net increase in energy. Consequently, the electrons placed in this molecular orbital lead to a destabilization of the molecule and that is why this orbital is said to be antibonding.

It needs to be pointed out that the energy of the antibonding orbital is raised above the energy of the atomic orbitals that have combined by an amount more than that by which the energy of the bonding orbital has been lowered. The total energy for two molecular orbitals however remains the same as that of the two original atomic orbitals.

Types of Molecular Orbitals

In case we are considering the bonding in two similar atoms (homonuclear) then the magnitude of their coefficients C and C must be the same. In that case

$$C^2$$

There will be two molecular orbitals as a result of two types of combinations. These may be written as

$$\psi^b = \quad \text{as } C \text{ and } C \text{ are equal in magnitude}$$
$$\psi^a = \psi_A + \psi_B \quad \text{values have opposite sign}$$

The number of molecular orbitals is always equal to the number of atomic orbitals involved in bonding. The effective combination of atomic orbitals to form stable molecular orbitals requires:

(i) The symmetry and energy of atomic orbitals ψ_A and ψ_B must be close to each other.

(ii) The extent of overlap between the charge clouds of the orbitals should be large.

(iii) Atomic orbitals of the same sign should overlap.

Bonding and antibonding molecular orbitals. The molecular orbital that is obtained by the addition overlap (*i.e.*, when the lobes of the orbitals combine with the same sign) of two atomic orbitals is termed the bonding molecular orbital and is represented as ψ^b.

$$\psi^b = \psi_A + \psi_B$$

(a) Some salient features of bonding molecular orbital are:

(i) It possesses lower energy than the atomic orbitals from which it is formed.

(ii) It has high electron density in the region between the two nuclei and this accounts for the stability of the bond.

(iii) It is formed when the lobes of the combining atomic orbitals have the same sign. The magnitude of ψ^b is numerically bigger than ψ_A or ψ_B.

Every electron in a bonding MO contributes to attraction between two atoms.

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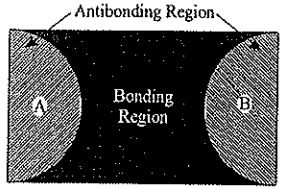

The other molecular orbital which is obtained by the subtraction overlap (*i.e.*, when the lobes of atomic orbitals overlap with opposite signs) of two atomic orbitals is termed the antibonding molecular orbital and is represented as ψ^a

$$\psi^a = \psi_A - \psi_B$$

(b) Some salient features of antibonding molecular orbital are:

(i) It possesses higher energy than the atomic orbitals from which it is formed.

(ii) The probability of finding the electron in between the nuclei is negligible. The electron density is concentrated only on one nucleus at any given instant.

(iii) It is formed when the lobes of the combining atomic orbitals have opposite signs. ψ^a is numerically smaller than ψ_{BO}.

(iv) Every electron in an antibonding molecular orbital contributes to repulsion between two atoms.

Comparison of Bonding and Antibonding Molecular Orbitals

Bonding Molecular Orbital	Antibonding Molecular Orbital
1. It possesses lower energy than atomic orbitals from which it is formed.	1. It possesses higher energy than the atomic orbitals from which it is formed
2. There is greater electron density between the nuclei of bonded atoms.	2. There is less electron density between the nuclei of bonded atoms.
3. Every electron in bonding molecular orbital contributes to the attraction between the two atoms..	3. Every electron in antibonding molecular orbital contributes to the repulsion between the atoms.
4. It results by the addition overlap of atomic orbitals.	4. It results by the subtraction overlap of atomic orbitals.
5. It favours the formation of bond.	5. It does not favour the formation of bond.

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Labelling of Molecular robitals

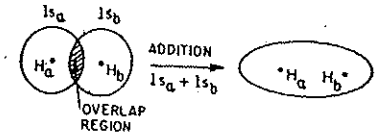
Just we we define atomic **orbitals** by letters *s, p, d* depending upon their shapes, so in a similar fashion, letters σ, π, δ, etc. (Greek letters) are used to characterize the different shapes of electron clouds in molecules (molecular orbitals).

(a) σ-Molecular Orbitals :

The addition or subtraction combination of s atomic orbitals centred on two nuclei produces molecular orbitals which have cylindrical symmetry around the bond axis. *Molecular orbitals with cylindrical symmetry are called* σ (*sigma*) *molecular orbitals.*

We may demonstrate their formation by combining two 1s atomic orbitals belonging to, say two hydrogen atoms. Using the LCAO approach the two atomic orbitals will overlap to give two molecular orbitals. The first combination is obtained by the addition of two atomic orbitals. The pictorial representation is shown in.

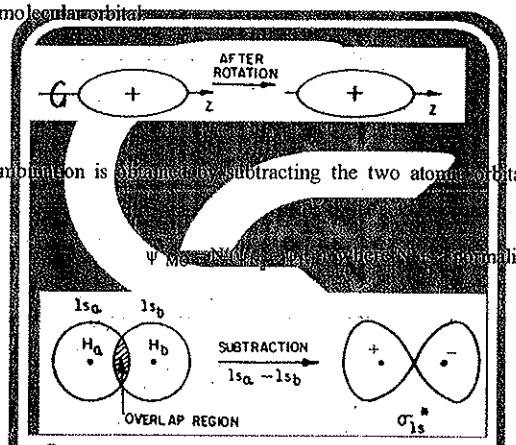
$\psi^b MO = N(\psi_{1s_a} + \psi_{1s_b})$, where N is a normalizing constant



The electron in this MO will spend most of its time between the two nuclei H_a and H_b. The electron is now stabilized by two nuclear charges instead of one unlike in an atomic orbital. The resulting MO is of lower energy than the 1*s* atomic orbital. That is why it is called a bonding MO.

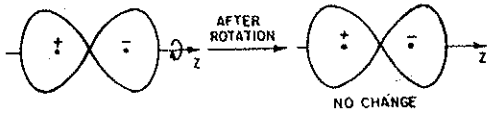
We may also observe that this molecular orbital is symmetric to rotation about the internuclear axis. It means that the MO is unaffected by rotation operation through 180°. An orbital which possesses this symmetry is called a sigma (σ) molecular orbital. The superscript '*b*' is attached to show that it is a sigma bonding (σ^b) molecular orbital.

The other linear combination is obtained by subtracting the two atomic orbitals and is shown in following figure.

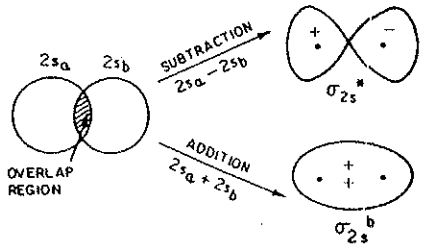


$\psi^* MO = N(\psi_{1s_a} - \psi_{1s_b})$, where N is another normalizing constant.

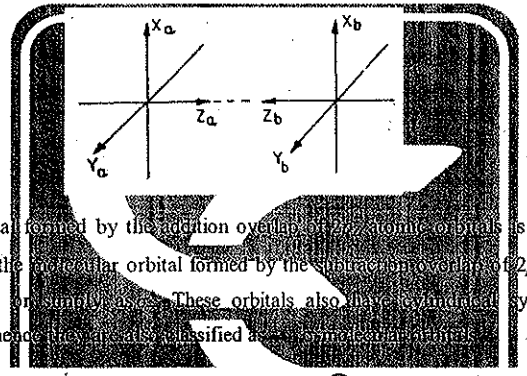
The *resulting molecular orbital has a nodal plane (region of zero electron density) between the two nuclei.* The electron in this orbital is concentrated in regions away from each nuclei. The net effect is to push the nuclei apart rather than to hold them together. The resulting molecular orbital is of higher energy than the isolated 1*s* atomic orbitals. The resulting molecular orbital is called an antibonding molecular orbital. It can be easily shown in following figure that this MO is also symmetric to rotation about the internuclear axis, *i.e.*, it has cylindrical symmetry. It is labelled as σ^a_{1s} or σ^*_{1s} meaning sigma antibonding molecular orbital.



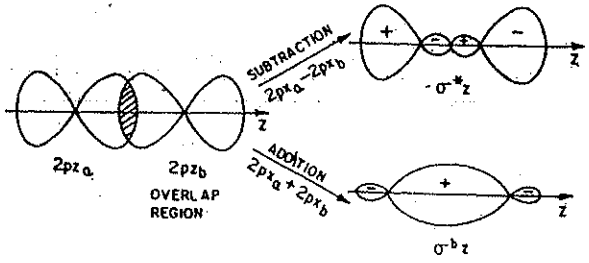
The combination of 2*s* atomic orbitals also gives rise to σ-molecular orbitals. The situation is exactly like the overlapping of 1*s* atomic orbitals. The only difference is that their sizes are different. Their overlap is illustrated in a diagram given below.



It may be pointed out that σ-type molecular orbitals are also formed when p_z atomic orbitals of two atoms combine with each other. We are now adopting a convention by assuming that the internuclear axis is the z-axis. This is illustrated in a diagram shown below.



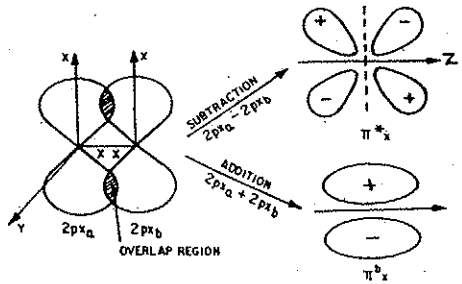
The molecular orbital formed by the addition overlap of $2p_z$ atomic orbitals is designed as σ^b_{2pz} or simply as σ^b_z while the molecular orbital formed by the subtraction overlap of $2p_Z$ atomic orbitals is designated as σ^*_{2pz} or simply as σ^*_z. These orbitals also have cylindrical symmetry around the molecular axis and hence they are also classified as σ-molecular orbitals.



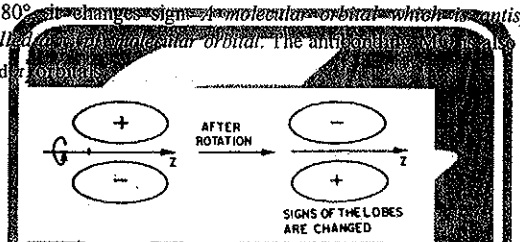
(b) π-Molecular Orbitals:

Molecular orbitals which are obtained by the lateral (or sidewise) overlap of p_x or p_y orbitals are designated as π (pi) molecular orbitals. This is illustrated by showing overlap of $2p_x$ atomic orbitals.

If the overlap contains the same algebraic signs, we get bonding MO and if these are of opposite sign we get antibonding MO.



The bonding molecular orbital has (+) lobe above the z-axis and (−) lobe below the z-axis. If we rotate this MO through 180° it changes sign. *A molecular orbital which is antisymmetric about the molecular axis is called a π molecular orbital.* The antibonding MO is also a π ntype MO. They are labelled as π^b_z and π^*_z orbitals.



The two $2py$ atomic orbitals will also overlap in a similar fashion to give π^b_y and π^*_y MO's. Both π_x and π_y molecular orbitals are equivalent and have the same energy. These orbitals, are said to be degenerate, *i.e.*, orbitals with the same energy.

(c) Comparison of σ- and π-overlap:

In a σ-overlap, the overlap density is much greater than in a π-overlap. The difference arises because in a σ-overlap the two orbitals involved head-on overlap, whereas in a π-overlap, the two orbitals π-overlap laterally (on side wise). This is shown in the following diagram.

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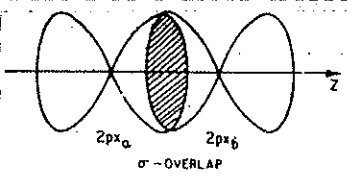
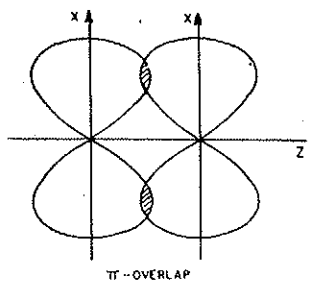




The net result is that a π-bond is a weaker bond than a σ-bond.

Important differences in σ and π-overlaps are given below:

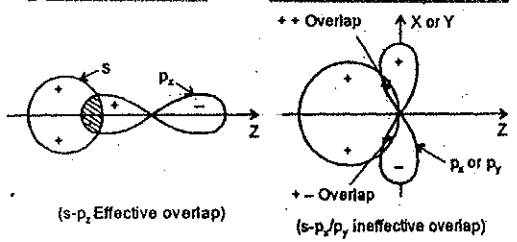
σ-overlap	π-overlap
It is formed by head on overlap of atomic orbitals.	It is formed by sideway (or lateral) overlap o atomic orbitals.
The overlap region is larger and greater than π-overlap	The overlap region is small.
It is a strong bond.	It is usually weak.
It is symmetrical to rotation about molecular axis.	It is a antisymmetric to rotation about molecula axis.

(d) Effective Combinations of Atomic Orbitals:

1. Combining orbitals should have similar energies. All orbitals can't combine with each other.Only those combinations are effective where the energies match. For example, energy of 1*s* orbital of H atom matches with 2*p* orbital of F with the result that such an overlap is possible to form HF.

2. Combining orbitals should overlap effectively. Effective overlap leads to stable bond formation. Only those overlaps are effective where the extent of overlapping is large.

3. Combining orbitals must have similar symmetries along internuclear axis. An *s*-orbital can combine with another *s*-orbital if conditions (1) and (2) are satisfied. Similarly a p_z orbital can combine with a p_z orbital provided conditions (1) and (2) are satisfied. However, a p_z orbital cannot combine with a p_x or p_y orbital because they do not have similar symmetries about internuclear axis. Also an *s*-orbital can combine with a p_z orbital effectively whereas such a combination with p_x or p_y orbital is not effective as shown below:



In case of *s* p_x or p_y overlap (shown on RHS), the + + overlap is cancelled by + – overlap. In other words, it is an ineffective overlap and no MO is formed. Such a combination is, therefore, not permissible and called zero overlap.

As shown in LHS, the *s* p_z overlap (*z* is molecular axis) is a ++ overlap and hence effective. Both *s* and p_z have the same symmetry about internuclear z-axis.

The following combinations are **symmetry permissible** taking z as internuclear axis:

$$s - s; s - p_z; p_z - p_z; p_y - p_y, p_x - p_x$$

The following combinations are **not symmetry permissible:**

$$s - p_x \text{ or } p_y; p_z - p_x \text{ or } p_y$$

Thus we may conclude that on the basis of symmetry, the allowed and forbidden combinations of various atomic orbitals are as follows, assuming z-axis as the internuclear axis.

Orbital	Allowed Combinations	Forbidden Combinations	Type of Molecular orbitals formed
s	$s - s; s - p_z$	$s - p_x; s - p_y$	σ, σ*
p_x	$p_x - p_x$	$p_x - p_y; p_x - p_z$	π, π*
p_y	$p_y - p_y$	$p_x - p_y; p_x - p_z$	π, π*
p_z	$s - p_z; p_z - p_z$	$p_x - p_z; p_y - p_z$	σ, σ*

Rules for Linear Combination of Atomic Orbital

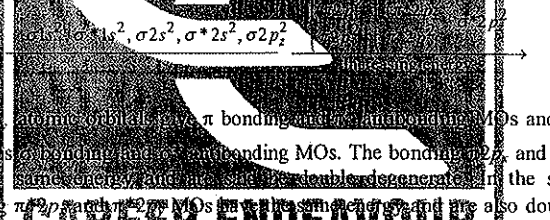
(1) The atomic orbitals must be roughly of the same energy.

(2) The orbitals must overlap one another as much as possible, *i.e.*, atoms must be close enough for effective overlap and that the radial distribution function of two atoms must be similar at this distance.

(3) In order to produce bonding and antibonding MOs, either the symmetry of the two atomic orbitals must remain unchanged when rotated about the internuclear line or both atomic orbitals must change symmetry in an identical manner.

(4) Pauli Exclusion Principle applies to molecules also. No two electrons in the same molecule can have all four quantum numbers the same.

The order of the energy of molecular orbitals has been determined mainly from spectroscopic data. In simple homonuclear diatomic molecules the order is:



$2p_x$ and $2p_y$ atomic orbitals give π bonding and π* antibonding MOs and the $2p_z$ atomic orbital gives σ bonding and σ* antibonding MOs. The bonding $\pi 2p_x$ and $\pi 2p_y$ MOs have exactly the same energy and hence they are double degenerate. In the similar way the antibonding $\pi^* 2p_x$ and $\pi^* 2p_y$ MOs have the same energy and are also doubly degenerate. The energies of the σ2*p* and π2*p* MOs are very close together. The order of MOs shown above is correct for oxygen and heavier elements but for lighter elements boron, carbon and nitrogen the $\pi 2p_x$ and $\pi 2p_y$ are probably lower than $\sigma 2p_z$. For these atoms the order is:

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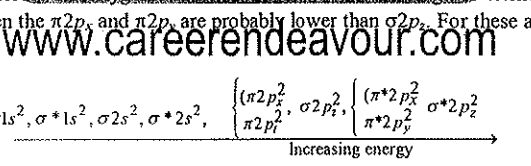
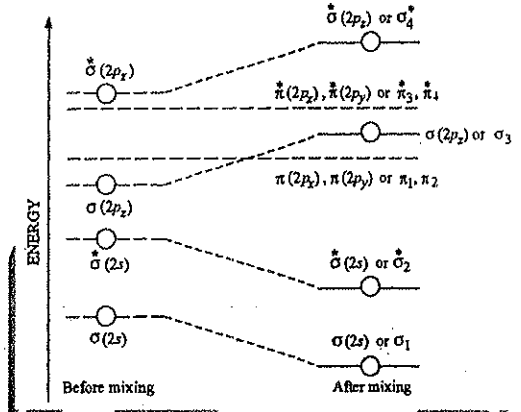


Mixing of Orbitals

We have seen that σ(2*s*) and σ*(2*s*) MOs are formed by the combination of 2*s* atomic orbitals of two atoms while σ(2p_z) and σ*(2p_z) MOs are formed by the combination of 2p_z atomic orbitals of the two atoms. However, if the energy differences between 2*s* and 2*p* atomic orbitals are small, there is a possibility of **mixing** of molecular orbitals σ(2*s*) with σ(2p_z) as they are of the same symmetry and σ*(2*s*) with σ*(2p_z) as they are also of the same symmetry with the result that the σ(2*s*) and σ*(2*s*) MOs do not retain the pure *s* character and the σ(2p_z) and σ*(2p_z) MOs do not retain the

pure p character. In fact, all the four MOs acquire a mixed sp character. Due to this s-p mixing, the energies of all the four orbitals change in such a way that the resulting MOs $\sigma(2s)$ and $\sigma^*(2s)$, which also contain some p character, become more stable and are thus lowered in energy whereas the MOs $\sigma(2p_z)$ and $\sigma^*(2p_z)$ which contain some s character also now become less stable and are thus raised in energy, as illustrated in following figure.



Since $\pi(2p)$ orbitals are not involved in mixing, the energies of $\pi(2p_x)$ and $\pi(2p_y)$ MOs remain unchanged, as shown in the figure.

As can be seen from above figure, $\sigma(2p_z)$ MO is raised to such an extent that it becomes higher in energy than $\pi(2p_x)$ and $\pi(2p_y)$ MOs. The new sequence of energy of MOs, therefore, becomes

$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_x) = \pi(2p_y) < \sigma(2p_z) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$

Energy →

In the above sequence $\pi(2p_x)$ and $\pi(2p_y)$ MOs are degenerate (have same energy) orbitals.

Now, a question arises: How is it that the mixing of $\sigma(2s)$ with $\sigma(2p_z)$ or of $\sigma^*(2s)$ with $\sigma^*(2p_z)$ occurs in the case of second row elements upto nitrogen only and not in the case of oxygen and fluorine. The answer lies in the difference in energies of 2s and 2p atomic orbitals of atoms of second row elements.

The differences in energies of $2s$ and $2p_z$ atomic orbitals of atoms up to nitrogen are small. Therefore, the energy differences between BMOs $\sigma(2s)$ and $\sigma(2p_z)$ [and between ABMOs $\sigma^*(2s)$ and $\sigma^*(2p_z)$] is also small upto N_2. Since $\sigma(2s)$ and $\sigma(2p_z)$ are of the same symmetry, these would mix effectively with each other and energies of the resulting mixed molecular orbitals would be considerably different from the energies of pure $\sigma(2s)$ and pure $\sigma(2p_z)$ molecular orbitals. A similar situation occurs in the case of molecular orbitals obtained by mixing of $\sigma^*(2s)$ with $\sigma^*(2p_z)$ molecular orbitals of molecules upto N_2.

In the case of O_2 and F_2, however, the energy differences between $2s$ and $2p$ atomic orbitals are quite large. Consequently, the energy differences between $\sigma(2s)$ and $\sigma(2p_z)$ or between $\sigma^*(2s)$ and $\sigma^*(2p_z)$ molecular orbitals in case of O_2 and F_2 are also quite large with the result that neither $\sigma(2s)$ and $\sigma(2p_z)$ nor $\sigma^*(2s)$ and $\sigma^*(2p_z)$ can mix to any significant extent in these molecules. Hence the energies of $\sigma(2s)$, $\sigma(2p_z)$, $\sigma^*(2s)$ and $\sigma^*(2p_z)$ molecular orbitals practically remain unaltered so that

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the energy of $\sigma(2p_z)$ molecular orbital continues to remain lower than the energies of $\pi(2p_x)$ and $\pi(2p_y)$ molecular orbitals.

Factors on Which Bond Energy Depends

1. Bond Length : Shorter the bond length, greater is the bond energy. For example,

	C—C	C = C	C ≡ C
Bond length (pm)	154	134	120
Bond energy (kJ mol^{-1})	347.2	615.0	811.6

2. Size of Bonded Atoms : Shorter the size of bonded atoms, greater is the bond energy. Thus, bond energy values decrease down the group. For example,

	Li—Li	Na—Na	K—K
Bond energy (kJ mol^{-1})	108.7	75.3	54.3

3. Bond Order : Bond energy increases as the bond order increases. This is evident from above where C ≡ C has greater bond energy than C = C bond which has greater bond energy than C—C bond.

4. Electronegativity: The greater the electronegativity difference between the bonded atoms, greater is the bond energy. For example

	HF	HCl	HBr	HI
Electronegativity difference	1.9	0.9	0.7	0.3
Bond energy (kJ mol^{-1})	568.1	431.8	366.1	298.3

5. Number of Lone Pairs : The greater the number of lone pairs on the bonded atoms, the greater is the repulsion between them. This results in a weaker bond. Hence bond energy decreases. For example,

	C—C	N—N	O—O
Bond energy (kJ mol^{-1})	347.2	158.9	142.2

6. Hybridisation: The bond formed by hybridised orbitals is greater than that of unhybridised orbitals. Therefore, hybridised orbitals from stronger bonds and have higher bond energy than the unhybridised orbitals. As the percentage of p-character in the hybridised orbitals increases, the bond energy increases. Hence, order of bond energy is as follows:

$$sp^3 > sp^2 > sp > p > s$$

7. Bond Angle : The greater the bond angle, the greater is the bond energy. For example, order of bond energies is as follows:

	BeF_2	>	BF_3	>	CCl_4
Bond angle	180°		120°		109°, 28°

MOT for Homonuclear Diatomic Molecules

H_2^+ Molecular Ion: This way considered as a combination of a H atom with a H^+ ion. This gives one electron in the molecular ion which occupies the lowest energy.

$$MO: \rightarrow \sigma 1s^1$$

The electron occupies the σ1s bonding MO. The energy of this ion is thus lower than that of the constituent atom and ion by an amount Δ and so there is some stabilization. This species is exist but not common since H_2 is much more stable. However H_2^{2+} can be detected spectroscopically when H_2 gas under reduced pressure is subjected to an electric discharge.

H_2 Molecule: → There is one electron from each atom and hence there are two electrons in the molecule, these occupy the lowest energy MO $\sigma 1s^2$.

The bonding σ1s MO is full, so that stabilizing energy is 2Δ. A σ bond is formed, and the H_2 molecule exists and is well known.

Bond Order:

$$= \left\{\frac{\text{No. of Electrons occupying bonding orbitals} - \text{No. of Electron occupying antibonding orbitals}}{2}\right\}$$

$$= \frac{2-0}{2} = 1$$

He_2^+ Molecule Ion: This may be considered as a combination of a He atom and a He^+ ion. There are three electrons in the molecular ion which are arranged in MOs: $\sigma 1s^2, \sigma^* 1s^1$. The filled σ1s bonding MO gives 2Δ stabilization whilst the half filled σ*1s gives Δ destabilization. Overall there is Δ stabilization, thus the helium molecule ion can exist but is more stable but can observed spectroscopically.

$$\text{Bond order} = \frac{2}{2}$$

He_2 Molecule → There are two electrons from each atoms are four electrons arranged in MOs: $\sigma 1s^2$, $\sigma^* 1s^2$ the 2Δ stabilization energy from filling the σ1s MO is cancelled by the 2Δ desabilization energy from filling the σ*1s MO. Thus no bond is formed and molecule does not exist.

$$\text{Bond order} = \frac{2-2}{2} = 0$$

Li_2 Molecule: → Each lithium atom has three electrons with one in its outer shell giving three electrons thus there are a total of six electrons in the molecule and these are arranged in MOs: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$. The inner shell of filled σ1s MO and σ*1s do not contribute to bonding in much the same way as in He_2. They are essentially the same as the atomic orbitals from which they are formed and sometimes written as KK $\sigma 2s^2$. However bonding occurs from the filling of the σ2s level, and Li_2 molecules do exist in the vapour state.

However, in the solid it is energetically more favorable for lithium to form a metallic structure.

$$\text{Bond Order} = \frac{4-2}{2} = 1.$$

Be_2 Molecule: → A Be atom has two electrons in the 1st shell plus two electrons in the second shell. Thus in the Be_2 molecule there are eight electrons. These are arranged in MOs: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, the inner shell of σ1s MOs does not contribute to the bonding.

The 2Δ stabilizing energy from filling the σ2s MO is cancelled by the 2Δ destabilization energy from filling the σ*2s MO, so there is no stabilization and the molecule would not be expected to exist.

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O_2 Molecule : Each oxygen atom has 2 + 6 = 8 electrons. Thus the O_2 molecule contains a total of 16 electrons. These are arranged in MOs: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2p_z^2 \begin{cases} (\pi 2p_y^2, & \begin{cases} (\pi^* 2p_y^1 \\ \pi 2p_x^2, \end{cases} & \pi^* 2p_x^1 \end{cases}$

The antibonding $\pi^* 2p_x$ and $\pi^* 2p_y$ orbitals are singly occupied in accordance with Hund's rule. Unpaired electron rive rise to paramagnetism. Since there are two unpaired electrons with parallel spins, this explains why oxygen is paramagnetic. If this treatment is compared with the Lewis electron pair theory or the valence bond theory, these do not predict unpaired electrons or paramagnetism.

This was the first success of the molecular orbital theory in successfully prediciting the paramagnetism of O_2, a fact not even thought of with a valence bond representation of O = O.

A σ bond results from the filling of $\sigma_{2p_z}^2$. Since $\pi_{2p_y}^{*1}$ is half filled and therefore cancels half the effect of the complete the filled $\pi 2p_y^2$ orbitals, half of a π bond results. Similarly another half of a π bond arises from $\pi 2p_x^2$ and $\pi^* 2p^1$ giving a total of 1 + ½ + ½ = 2 bonds. The bond order is thus two.

$$\text{B.O.} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 6] = 2$$

O_2^- Ion : The O_2^- ion has 17 electrons and has one more electron than the O_2 molecule. The extra electron occupies either the $\pi^* 2p_y$ or $\pi^* 2p_x$ orbitals.

Bond Order = (10 – 7)/2 = ½ and it is paramagnetic in nature due to an unpaired electron.

O_2^{2-} ion : This ion has 18 electrons, arranged like

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2 \begin{cases} (\pi 2p_y^2 \\ \pi 2p_x^2 \end{cases} \begin{cases} (\pi^* 2p_y^2 \\ \pi^* 2p_x^2 \end{cases}$$

Bond order (10 – 8)/2 = 1, diamagnetic in nature.

F_2 molecule

Fluorine atoms have 2 + 7 = 9 electrons so F_2 molecule contains 18 electrons. These are arranged:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2 \begin{cases} (\pi 2p_y^2 \\ \pi 2p_x^2 \end{cases} \begin{cases} (\pi^* 2p_y^2 \\ \pi^* 2p_x^2 \end{cases}$$

The inner shell is non-bonding and the filled bonding $\sigma 2s$, $\pi 2p_x$ and $\pi 2p_y$ are cancelled by the equivalent antibonding orbitals. This leaves a σ bond from the filled $\sigma 2p_z^2$ orbital and thus a bond order of one. Alternatively, bond order = (electrons in bonding – electrons in antibonding)/2, that is (10 – 8)/2 = 1.

It should be noted that Cl_2 and Br_2 have structures analogous to F_2, except that additional inner shells of electrons are full.

The F—F bond is rather weak and this is attributed to the small size of fluorine and repulsion between lone pairs of electrons on adjacent atoms.

Molecular Orbital Treatment for Heteronuclear Diatomic Molecules

The same principles apply when combining atomic orbitals from two different atoms as applied when the atoms were identical, that is:

1. Only atomic orbitals of about the same energy can combine effectively.
2. They should have the maximum overlap.
3. They must have the same symmetry.

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Since the two atoms are different, the energies of their atomic orbitals are slightly different. The problem is that in many cases the order of MO energy levels in not known with certainty.

NO Molecule: The nitrogen atom has 2 + 5 = 7 electrons, and the oxygen atom has 2 + 6 = 8 electrons, making 15 electrons in the molecule. The order of energy levels of the various MOs are the same as for homonuclear diatomic molecules heavier than C_2.

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2 \begin{cases} (\pi 2p_x^2 \\ \pi 2p_y^2 \end{cases}, \begin{cases} (\pi^* 2p_x^1 \\ \pi^* 2p_y^0 \end{cases}$$

The inner shell is non-bonding

Bond order = (10 – 5)/2 = 2 ½, paramagnetic

For NO^+ removal of an electron from NO gives NO^+ ion. The electron is removed from π^* antibonding M.O. to give configuration

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2 \begin{cases} \pi 2p_x^2 \\ \pi 2p_y^2 \end{cases}$$

$$\text{B.O} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 4]$$

It is diamagnetic

CO Molecule: The CO molecule has 14 electrons.

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \begin{cases} \pi 2p_x^2 \\ \pi 2p_y^2 \end{cases} \sigma 2p_z^2$$

$$\text{B.O.} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 4] = 3$$

The inner shell is non-bonding, and the bonding and antibonding 2*s* orbitals cancel, leaving one σ and two π bonds and thus a bond order of 3. This simple picture is inadequate, since if CO is ionized to give CO^+ by removal of the electron from the $\sigma 2p_z$ orbital then the bond order should be reduced to 2 ½ and bond length increased. But bond length of CO is 1.128 Å and in CO^+ it is 1.115 Å. The most likely explanation of the bond shorting when CO is changed to CO^+ is that σ^*2s MO is higher in energy then the $\sigma 2p_z$, $\pi 2p_x$ and $\pi 2p_y$ MOs.

Thus the above electronic configuration is incorrect for CO^+.

Since atomic orbitals of O are lower in energy than the corresponding orbitals of C and this difference is large, therefore, the bonding molecular orbitals are more like the atomic orbitals of O.

The electronic configuration of CO molecule is:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma 2p_z^2 \ \pi 2p_x^2 = \pi 2p_y^2 \ \sigma^* 2s^2$$

$$\text{B.O.} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 4] = 3$$

CO^+ ion : The M.O. configuration of CO^+ can be derived from CO by removing an electron from HOMO σ^*2s

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2 \ \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2 \ \sigma^* 2s^1$$

$$\text{B.O.} = \frac{10 - 3}{2} = 3.5$$

This shows that B.O. increases in CO^+ compared to CO. This is supported by the bond distance which is shorter in CO^+ compared to CO.

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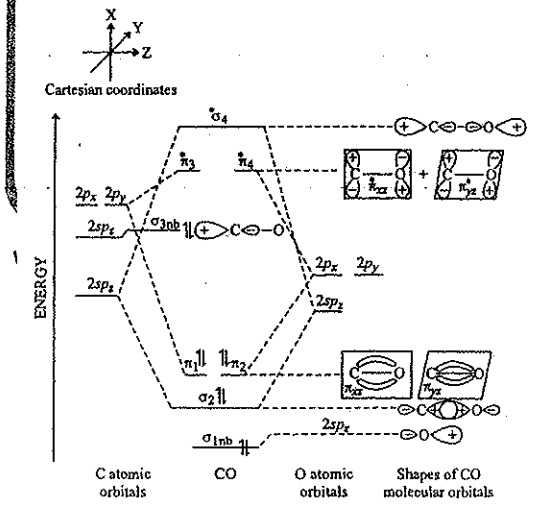
Bond distance for CO^+ = 1.115 Å

Bond distance for CO = 1.128 Å

Coulson Method:

The electronic configurations of C and O atoms are $1s^2 2s^2 2p^2$ and $1s^2 2s^2 2p^4$, respectively. There are 4 electrons in the outer shell of carbon and 6 electrons in the outer shell of oxygen. Thus, a total of 10 outer electrons are to be accommodated in the molecular orbitals of CO molecule. Because of higher electronegativity of oxygen, its atomic orbitals would be of lower energy than the corresponding atomic orbitals of carbon. Due to this energy difference, the bonding and antibonding molecular orbitals receive different contributions from atomic orbitals of carbon and oxygen. The bonding molecular orbitals receive more contribution from atomic orbitals of lower energy, *i.e.*, the atomic orbitals of oxygen and would be closer to it in energy than the antibonding molecular orbitals which would be closer to the atomic orbitals of carbon in energy, as shown in following figure. The bonding molecular orbitals would have more characteristics of atomic orbitals of oxygen and antibonding molecular orbitals would have more characteristics of atomic orbitals of carbon.

The 2*s* and 2p_z atomic orbitals of C atom mix to produce two atomic orbitals of mixed sp_z character. The higher energy mixed sp_z orbital of C atom is close in energy to its pure 2p_z orbital and has major contribution from it whereas the lower energy mixed sp_z orbital of C is closer in energy to its pure 2*s* orbital and has major contribution from it. Similarly 2*s* and 2p_z atomic orbitals of oxygen atom also mix with each other (though not to the same extent to which the orbitals of C atom mix because the energy difference between 2*s* and 2p_z atomic orbitals of oxygen atom is higher than that between the similar atomic orbitals of C atom) to form two atomic orbitals of mixed sp_z character. The higher energy mixed sp_z orbital of O is very close in energy to its pure 2p_z orbital and has contribution mostly from 2p_z orbital whereas the lower energy mixed sp_z orbital is very close in energy to pure 2*s* orbital of oxygen atom and has contribution mostly from 2*s* orbital of oxygen atom.



Since the orbital energies are lower for more electronegative O atom compared to the energies of similar orbitals of C atom, the lower energy mixed sp_z orbital of C atom is comparable in energy to the higher energy sp_z orbital of O atom, as shown in MOEL diagram of CO. These two atomic orbitals of comparable energy and of same symmetry combine to give σ bonding and antibonding molecular orbitals. The lower energy sp_z, orbital on O and the higher energy sp_z orbital on C atom are

so far apart in energy that they *hardly* influence each other with the result that their energies remain almost unchanged. In other words, these orbitals remain *almost* non bonding. the non bonding sp_z orbital on C (σ_{3nb} in the figure) will have more characteristics of $2p_z$ orbital of C atom and the non bonding sp_z orbital on C (σ_{3lb} in the figure) will have more characteristics of $2s$ orbital of O atom. The degenerate set of $2p_x 2p_y$ orbitals of C and the similar degenerate set of $2p_x 2p_y$ orbitals of oxygen are of π symmetry to form a set of degenerate π_1,π_2 bonding molecular orbitals and another set of degenerate antibonding molecular orbitals. The electronic configuration of CO molecule is, therefore,

$$KK'\sigma_{1nb}^2\,\sigma_2^2\,\pi_1^2 = \pi_2^2\,\sigma_{3nb}^2$$

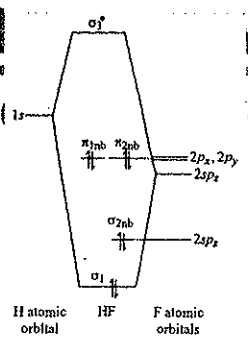
and the **bond order** of CO molecule is obviously 3 (due to two σ bonding and four π bonding electrons. The electrons in the non bonding-orbitals do not contribute towards bonding.

Since σ_{3nb} is the highest placed occupied non bonding orbital localised on C atom, its electron pair can easily be donated for forming dative (or coordinate) bond.

Hydrogen Flouride Molecule, HF

The valence shell atomic orbitals of the same symmetry are 1s atomic orbital of H and $2s$ and $2p_z$ atomic orbitals of F (the z axis is assumed to be the internuclear axis). The two $2s$ and $2p_z$ of F, being of the same symmetry, can mix with each other. However the extent of mixing of $2s$ and $2p_z$ orbitals will be *small* because the energy gap between these two orbitals is *high*. (For effective mixing of orbitals of same symmetry, the energy gap between them should be low).

The higher energy mixed orbital of F has predominantly $2p_z$ character with very little s character and will lie only *a little lower* in energy than the pure $2p_z$ orbital. Similarly, the lower energy mixed orbital has predominantly $2s$ character with only a little $2p_z$ character and lies *slightly higher* in energy than the pure $2s$ orbital. The 1s orbital of hydrogen atom is much comparable in energy to the higher energy mixed sp_z orbital (which is practically $2p_z$ orbital). These two combine to give σ_1 bonding and σ_3^* antibonding molecular orbitals. The lower energy mixed $2s$ orbital of F *cannot effectively combine* with 1s orbital of H atom due to large energy difference between this mixed orbital and 1s orbital of H atom and therefore, remain *almost* non bonding (σ_{2nb}) orbital. The molecular orbital energy level diagram is shown in following figure.



The $2p_x$ and $2p_y$ orbitals of F are suitable for forming only π bonding and antibonding molecular orbitals. Since there are no orbitals of the same symmetry as that of H atom, these remain non bonding and are designated in the figure as π_{1nb} and π_{2nb}. It is clear from the above discussion that σ_1 will have more contribution from $2p_z$ atomic orbital of F and less contribution from $2s$ atomic orbital

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of F atom whereas σ_3^* will have more contribution from 1s orbital of H atom and less contribution from $2p_z$ orbital of H atom. The electronic configuration of HF molecule is thus,

$$K\,\sigma_1^2\,\sigma_{2nb}^2\,\pi_{1nb}^2 = \pi_{2nb}^2$$

and the **bond order** is obviously 1 since only two electrons occupy the bonding molecular orbital σ_1 (the rest of the valence electrons are in non bonding orbitals).

Hydrogen Chloride Molecule, HCl

The treatment in this case is exactly similar to the one discussed for HF molecule except for the fact that the valence shell atomic orbitals of the same symmetry that are considered for the formation of molecular orbitals, are $1s$ atomic orbital of H atom and $3s$ and $3p_z$ orbitals of Cl atom. The electronic configuration of HCl molecule is:

$$KL\,\sigma_1^2\,\sigma_{2nb}^2\,\pi_{1nb}^2\,\pi_{2nb}^2$$

and the **bond order** is one due to two electrons in bonding molecular orbital. In the case of HCl molecule also, all the molecular orbitals are either pure Cl orbitals or have predominantly Cl orbital character. Therefore, most of the electronic charge gets accumulated on Cl atom of HCl making it considerably polar.

Term Symbols for Diatomic Molecules

Term symbols are used to designate electronic energy levels which arise out of an electronic configuration because of electrostatic repulsions among the electrons of a molecule. These terms are very helpful in understanding electronic spectra of molecules.

The term symbols employed for diatomic molecules are written in the following manner:

1. The symbols Σ,π and Δ are used to represent values 0, 1 and 2 respectively for $|M_L|$ or Σm_l of electrons in the diatomic molecule, where m_l is the component of orbital angular momentum of a single electron along the internuclear axis and M_L is the absolute value or similar overall component for all the electrons in the diatomic molecule. The m_l is 0, ± 1 and ± 2 for an electron in σ, π and δ molecular orbitals, respectively.

2. Since all homonuclear diatomic molecules have a centre of symmetry in the middle of their nuclear axis, the overall symmetry to inversion is indicated by g or u, the symbol written as a right subscript of Σ,π,Δ.

3. The electron spin multiplicity is indicated by $2S + 1$ as the left superscript of Σ,π and Δ (S is the total spin of electrons in the system).

4. The term symbol is written as $^{2s+1}|M_L|_{g \text{ or } u}$.

For example, consider a H_2 molecule whose ground state electronic configuration is σ^2 (ls).

In this case, S (*i.e*, $s_1 + s_2$) is 0 and $|M_L|$, *i.e.*, $(m_{l_1} + m_{l_2})$ is also 0. The σ_{1s} molecular orbital is symmetric with respect to the centre of inversion located in the middle of the nuclear axis, Therefore, the term symbol for σ_{1s}^2 should be $g \times g = g$ type. Hence, the term symbol $^{2s+1}M_{Lg \text{ or } u}$ for H_2 molecule in its ground state, is $^1\Sigma_g$.

Consider now hydrogen ion, H_2^+. Its ground state electronic configuration is σ_{1s}^1 so that $S = \frac{1}{2}$ and $2S + 1 = 2$. Since $|M_L| = 0$, hence the term symbol for its ground state is $^2\Sigma_g$.

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Let us now work out the term symbols for O_2 molecule. The ground state electronic configuration of O_2 is. $\sigma_1^2 \sigma_2^2 \sigma_3^2 \pi_2^2 \pi_3^1 \pi_4^1$. The electrons in the filled sigma molecular orbitals and the completely filled degenerate set of pi orbitals contribute nothing to the overall component of angular momentum M_L along the nuclear axis. Since both the π^* molecular orbitals are symmetric with respect to the centre of symmetry of the oxygen molecule, the term symbol will be $g \times g = g$ type.

Let us first consider the case when both the unpaired electrons in π^* molecular orbitals have opposite spins. The m_l for each electron in π^* molecular orbital will be +1 or −1 so that $|M_L| = 0$ or 2 and $2S + 1 = 1$ (because $S = \frac{1}{2} - \frac{1}{2} = 0$). The term symbols which arise from this situation are ${}^1\Sigma_g$ *and* ${}^1\Delta_g$.

Now consider the case when the spins of both the electrons are in the same direction so that $S = \frac{1}{2} + \frac{1}{2} = 1$ and the spin multiplicity is 3. Since spins of both the electrons in π^* orbitals are in the same direction, their m_l values have to be different (Pauli's exclusion principle). That is, m_l for one electron is +1 and for the other electron it is −1 (The + and − signs indicate whether the component of angular momentum m_l is parallel or antiparallel to the nuclear axis). Therefore, $|M_L|$ can only be 0 so that the term is ${}^3\Sigma_g$.

Out of ${}^3\Sigma_g, {}^1\Sigma_g$ and Δ_g the first term ${}^3\Sigma_g$, having maximum multiplicity will evidently represent the ground state term of the molecule.

Terms for Li_2, Be_2, N_2 [illegible] molecules by yourself.

The term symbols for heteronuclear diatomic molecules are derived in a similar manner. Since a heteronuclear diatomic molecule has no centre of symmetry we do not write the subscript g or u in the term symbols of such molecules.

The Σ terms are sometimes further labelled by writing a + or − as a right hand superscript depending upon whether the system is symmetric or asymmetric with respect to a plane of symmetry passing through the nuclear axis.

Energy Levels of Molecular Orbitals

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$$

(For Li_2, Be_2, B_2, C_2, N_2)

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$$

(For O_2, F_2, Ne_2)

These energy levels can also be written as follow

$$\sigma_g(1s) < \sigma^*_u(1s) < \sigma_g(2s) < \sigma^*_u(2s) < \pi_u(2p_x) = \pi_u(2p_y) < \sigma_g(2p_z) < \pi^*_g(2p_x) = \pi^*_g(2p_y) < \sigma^*_u(2p_z)$$

(For Li_2, Be_2, B_2, C_2, N_2) (Mixing of σ_g orbitals)

$$\sigma_g(1s) < \sigma^*_u(1s) < \sigma_g(2s) < \sigma^*_u(2s) < \sigma_g(2p_z) < \pi_u(2p_x) = \pi_u(2p_y) < \pi^*_g(2p_x) = \pi^*_g(2p_y) < \sigma^*_u(2p_z)$$

(For O_2, F_2, Ne_2)

Gerade (g) orbital → Orbital symmetric to inversion.

e.g., If the molecular orbitals formed are symmetric to inversion (i.e., gerade), these orbitals are representing by using subscript 'g' such as σ_g and π_g. If the molecular orbitals formed are

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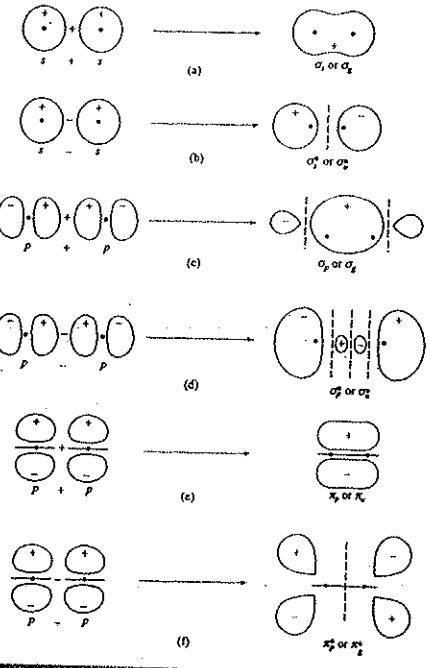
unsymmetric to inversion (i.e., ungerade), these orbitals are represented by using subscript 'u' such as σ_u and π_u.

The gerade and ungerade molecular orbitals are shown below.



Ionic Character

1. Electronegativity Difference Method

The amount of ionic character in A—B polar covalent bond indicates the extent to which the electron pair has shifted towards the more electronegative atom (extent of charge separation) in the bond. Greater is the electronegativity difference between the bonded atoms, A and B [*i.e.*, $(x_A - x_B)$, if $x_A > x_B$], greater will be the charge separation between the bonded atoms and hence greater will be the magnitude of ionic character in the bond. Several empirical equations have been proposed to calculate the amount of ionic character in A—B polar covalent bond. All these equations make use of electronegativity difference, $(x_A - x_B)$ Two of these equations are given below:

(a) Pauling's equation. According to Pauling, amount of ionic character is given by:

Amount of ionic character in A—B bond = $\left[1 - e^{0.25(x_A - x_B)}\right]\%$

Pauling suggested the following alternative empirical equation also for calculating the ionic character in A—B bond.

Ionic character in A—B bond = $\left[18(x_A - x_B)^{1.4}\right]\%$

Problem : On the basis of Pauling's equation calculate the percentage of ionic character in HF molecule, given that $x_F = 4.0$, $x_H = 2.2$.

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Solution. $x_F - x_H = 4.0 - 2.2 = 1.8$

Ionic character in HF molecule $= 18 \times (1.8)^{1.4}\% = 44.12\%$ ~~

This value (= 44.12%) is quite close to that (= 45%) obtained by Pauling from dipole moment of HF molecule.

(b) Hannay and Smith equation. These two chemists proposed the following equation to calculate the ionic character

$$\text{Ionic character in A—B bond} = \left[16(x_A - x_B) + 3.5(x_A - x_B)^2\right]\%$$

Problem : On the basis of Hanny and Smith equation, calculate the percentage of ionic character in gaseous HF, HCl, HBr and HI molecules, given that $x_F = 4.0$, $x_{Cl} = 3.2$, x_{Br}, $= 3.0$, $x_I = 2.7$ *and* $x_H = 2.2$

Solution. $x_F - x_H = 4.0 - 2.2 = 1.8$; $x_{Cl} - x_H = 3.2 - 2.2 = 1.0$; $x_{Br} - x_H = 3.0 - 2.2 = 0.8$;

$x_I - x_H = 2.7 - 2.2 = 0.5$

On putting the above values in Hannay - Smith's equation, we get

Ionic character in HF molecule $= [16 \times 1.8 + 3.5 \times (1.8)^2]\% =$ 40.14%

Ionic character in HCl molecule $= [16 \times 1.0 + 3.5 \times (1)^2]\% = 19.5\%$

Ionic character in HBr molecule $= [16 \times 0.8 + 3.5 \times (0.8)^2]\% =$ 15.04%

Ionic character in HI molecule $= [16 \times 0.5 + 3.5 \times (0.5)^2]\% =$ 8.875%

2. Dipole Moment Method

According to this method the percentage of ionic character in A—B bond in AB molecule is equal to

$$\frac{\mu_{exp}}{(\mu_{cal})_{ionic}} \times 100$$

$$= \frac{\mu_{exp}}{d_{A-B} \times \text{Electronic charge}} \times 100$$

Here μ_{exp} = Experimental (observed) or actual value of dipole moment of AB molecule

$(\mu_{cal})_{ionic}$ = Calculated (theoretical value) of dipole moment of AB molecule when this molecule is assumed to be completely ionic. The value of $(\mu_{cal})_{ionic}$ is calculated as follows :

$(\mu_{cal})_{ionic}$ = Distance between the centres of the positive and negative ends of $A^{\delta-} - B^{\delta+}$ dipole × Electronic charge.

$= d_{A-B} \times$ Electronic charge

Dipole Moment

If A—B bond in a AB molecule is polar (*i.e.*, AB is polar molecule), then AB molecule behaves as a dipole, since, it has two poles. The dipole can be represented as $A^{\delta-} - B^{\delta+}$ (when $x_A > x_B$) or $A^{\delta+} - B^{\delta-}$ (when $x_B > x_A$). Since the molecule as a whole is a neutral, one of the two ends of the dipole has a positive charge and the other end has a negative charge whose magnitude is the same as that of positive charge. These two charges are separated by a definite distance which is called bond length. If q is the charge (positive or negative) at each end of the dipole and l is the distance between the positive and negative charges i.e. l is the bond length), then the product of q and l is called dipole moment (μ) of AB molecule. Thus:

$$\mu = q \times l$$

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Units of Dipole Moment

If in a molecule an electron is assumed to be placed at a distance of 1Å from an equally positive charge, then the dipole moment (μ) of the molecule is given by:

μ = charge on the electron× Distance between the electron and the positive charge.

Now the charge on the electron in c.g.s. units is 4.8×10^{-10} electrostatic unit (*e.s.u*) while the charge on the electron in S.I. units is equal to 1.602×10^{-19} coulomb (C). Thus:

(a) μ *in c.g.s. units* $= (4.8 \times 10^{-10}\ esu) \times (10^{-8}\ \text{cm}) = 4.8 \times 10^{-18}\ esu.cm.$

Now the quantity $10^{-18}\ esu.cm$ is called one debye (D), *i.e.*, $10^{-18}\ esu.cm = 1\text{D}$

$\therefore \quad \mu = 4.8\ \text{D}$

Thus we find that in C.G.S units it is expressed in debye (D).

(*b*) μ in *S.I* units $= (1.602 \times 10^{-19}\ C) \times (10^{-8} \times 10^{-2}\ m)$ $= 1.602 \times 10^{-29}\ C.m$

Thus we find that in S.I. units it is expressed in coulomb meter (C.m) units.

Relation between Debye (D) and Coulomb-meter (C.m).

The dipole moment of a molecule in which electron is assumed to be placed at a distance of 1Å from an equally positive charge is equal to 4.8 D (in *c.g.s.* units) or 1.602×10^{-29} C.m (in *S.I.* units) Thus.

$4.8\text{D} = 1.602 \times 10^{-29}\ \text{C.m}$ or $1\text{D} = \frac{1.602 \times 10^{-29}\ \text{C.m}}{4.8}$

or $1\text{D} = 0.33 \times 10^{-29}\ \text{C.m}$

Also $1.602 \times 10^{-19}\ \text{C} \times 10^{-10}\ \text{m} = 1.602 \times 10^{-29}\ \text{C.m}$ or $1\text{C.m} = \frac{1}{1.602 \times 10^{-29}}\ \text{D}$

or $1\text{C.m} = 0.624 \times 10^{29}\ \text{D}$

Dipole Moment of A_2 (non-polar molecule) and AB Type Molecules

(a) A molecule of A_2 type (*e.g.* H_2, O_2, etc) is non-polar and contains one A—A bond. This molecule has zero dipole moment since both A atoms have the same electronegativity values.

(b) A molecule of AB type (*e.g.* HF, HCl, HBr, HI etc.) which contains A—B bond has a certain value of dipole moment, since A and B atoms have different values of their electronegativity.

Applications of Dipole Moment Values

1. To distinguish between polar and non-polar molecules. A molecule which has purely covalent bond is called non-polar molecule while that which contains polar covalent bond is called polar molecule. On the basis of the dipole moment value of a given molecule, it is possible to predict whether the given molecule is polar or non-polar in nature. The molecules having some value of dipole moment (*e.g.* HCN, OCS, NH_3, PF_3, AsF_3, H_2O, H_2S, SO_2, NO_2, O_3, N_2O etc.) are polar while those having zero value of dipole moment (*e.g.* CO_2, BeF_2, H_2, N_2, CH_4, SF_6, CS_2, BF_3, SO_3, CF_4, CCl_4 etc.) are non-polar. Greater is the value of dipole moment of a polar molecule, greater is the amount of ionic character in the polar covalent bond.

2. To calculate the percentage of ionic character in the polar covalent bond in a given molecule. Greater is the electronegativity difference between the bonded atoms in a polar molecule, greater is

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the value of dipole moment. Again we know that greater is electronegative difference, greater is % of ionic character in the bond linking the two atoms.

$$\text{Percentage of ionic character in A— B bond in AB molecule} = \frac{100 \times \mu_{exp}}{\mu_{ionic}}\%$$

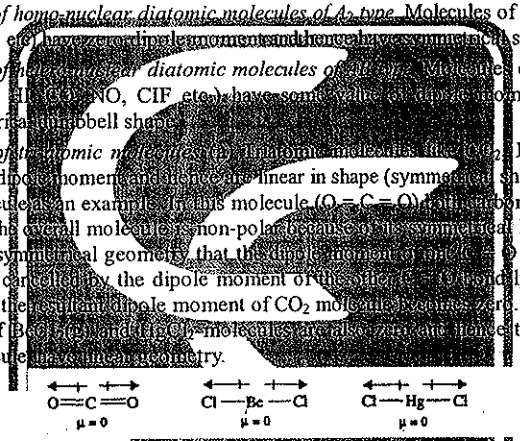
Here μ_{exp} = experimental (observed or actual) value of dipole moment of AB molecule, μ_{ionic} = calculated (theoretical) value of dipole moment of AB molecule when this molecule is assumed to be *completely ionic, i.e.*, an electron is completely transfered from less electronegative atom to more electronegative atom. Thus μ_{ionic} represents the dipole moment value for the ionic structure of AB molecule which can be represented as A^+B^- (when $x_B > x_A$) or as A^-B^+(when $x_A > x_B$).

3. To predict the shape of a given molecule. The dipole moment value of a given molecule can be used to predict whether the given molecule has symmetrical or unsymmetricl shape.

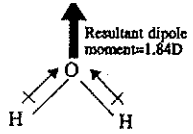
(i) Structure of homo-nuclear diatomic molecules of A_2 type. Molecules of this type (*e.g.* H_2,C_2, N_2 O_2, Cl_2 etc.) have zero dipole moments and hence have symmetrical shape (A—A).

(ii) Structure of hetero-nuclear diatomic molecules of AB type. Molecules of this type (*e.g.* HF, HCl, HBr, HI, CO, NO, ClF etc.) have some value of dipole moment and hence have unsymmetrical dumbbell shape (A—B).

(iii) Structure of tri-atomic molecules of AB_2 type. Tri-atomic molecules like CO_2, $BeCl_2$(g), $HgCl_2$ etc. have zero dipole moment and hence are linear in shape (symmetrical shape). Let us consider CO_2 molecule as an example. In this molecule (O = C = O) both carbon—oxygen bonds are polar but the overall molecule is non-polar because of its symmetrical linear geometry. It is due to its symmetrical geometry that the dipole moment of one C = O bond which is equal to 2.3D is cancelled by the dipole moment of the other C = O bond lying on the opposite side. Thus the resultant dipole moment of CO_2 molecule becomes zero. Similarly the dipole moment of $BeCl_2$(g) and $HgCl_2$ molecules are also zero and hence these molecules, like CO_2 molecule have linear geometry.

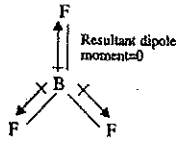


(b) Tri-atomic molecules like H_2O, H_2S, SO_2 etc. have some value of their dipole moment and hence have angular shape (unsymmetrical shape). For example, H_2O molecule has two indentical O—H bonds. Due to the unsymmetrical structure of the molecule, the dipole moments of two O—H bonds donot cancel each other and hence the net dipole moment of H_2O molecule is found to be equal to 1.84D. This value is the vector sum of dipole moments of two O—H bonds (each O—H bond has its dipole moment value equal to 1.5 D)

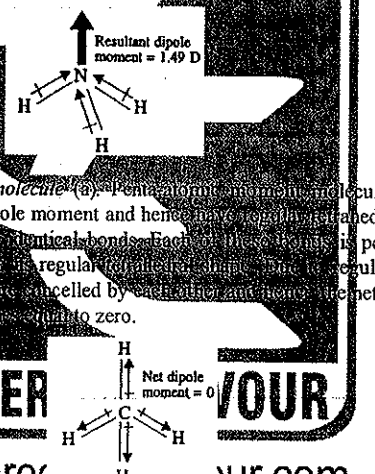


(iv) Structure of tetra-atomic molecules (a) Tetra-atomic molecules like BF_3, BCl_3, SO_3 etc. have zero dipole moment and have symmetrical trigonal geometry. Each of these molecules has three identical bonds. Let us consider BF_3 molecule as an example. This molecule has three B—F polar bonds but overall molecule is non-polar because of its symmetrical geometry. Due to the symmetrical geometry, the dipole moments of the three B—F bonds are cancelled by each other and hence the resultant dipole moment of BF_3 molecule

becomes equal to zero. On similar lines, zero dipole moment of BCl_3 and SO_3 molecules can also be accounted for.



(b) The tetra atomic molecules like NH_3, NF_3, PH_3, PCl_3 etc. have some value of their dipole moment and hence these molecules have trigonal pyramidal shape (unsymmetrical shape). Each of these molecules has three identical bonds. Although these bonds are identical, due to the unsymmetrical shape of the molecule, the dipole moments of the three bonds are not able to cancel each other and hence the net dipole moment of these molecules is not equal to zero, *i.e.*, they have some value of dipole moment. This value is the vector sum of the dipole moments of the three bonds.



(v) Structure of penta-atomic molecule (a) Penta-atomic tetrahedral molecules like CCl_4, CF_4, SiF_4, CH_4 etc. have zero dipole moment and hence have regular tetrahedral geometry. Each of these molecules has four identical bonds. Each of the bonds is polar but the overall molecule is non-polar due to its regular tetrahedral geometry. Due to regular shape the dipole moments of the four bonds are cancelled by each other and hence the net dipole moment of each of the molecules is found to be equal to zero.

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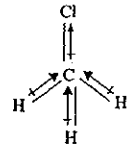
(b) Penta-atomic molecules like CH_3Cl has some value of dipole moment and hence has unsymmetrical tetrahedral structure. This has been explained as follows. This molecule has three C—H bonds and one C–Cl bond. Since all the four bonds are not identical, the dipole moments of these individual bonds are not able to cancel each other and hence the molecule has some value of its dipole moment and it has unsymmetrical tetrahedral structure.



Note :

(i) In a molecule which has symmetrical shape like *dumbbell*,(*e.g.* C_2, H_2, N_2, O_2, Cl_2, Br_2, etc.), *linear* (*e.g.* CO_2, $BeCl_2(g)$, $HgCl_2$), *trigonal planar* (*e.g.* BF_3, BCl_3, SO_3 etc.), *regular tetrahedral* (*e.g.* CH_4, CCl_4, CF_4 SiF_4 etc.), *trigonal bipyramidal* (*e.g.* PF_5, PCl_5 (g)), *square planar* (*e.g.* XeF_4), *regular octahedral* (*e.g.* SF_6, WF_6), *pentagonal bipyramidal* (IF_7) the dipole moments of the various bonds present in the molecule cancel each other and hence the net dipole moment of the molecule becomes equal to zero. Thus a molecule which has a symmetrical shape has no (zero) dipole moment.

(ii) In a molecule which has unsymmetrical shape like *angular* (*e.g.* H_2O, H_2S), *trigonal pyramidal* (*e.g.* NH_3, NF_3, PH_3 etc.) the dipole moments of the various bonds present in the molecule are not able to cancel each other and hence the molecule has some value for its dipole moment. Thus a molecule which has unsymmetrical shape has a certain value of dipole moment.

(4) To Calculate the bond angle between two bonds in a molecule. The angle subtended by two axes of overlaps of orbitals or bonds is called bond angle. The bond dipole moment vaues have been used to calculate the bond angle between two bonds. Bond angle (θ) between two bonds in a given molecule is given by the expression

Net dipole moment of the molecule =

in which m_1 and m_2 are the bond moments of various bonds present in the molecule.

Lattice Energy

Lattice energy (U) of a crystal is the energy released when one mole of an ionic crystal is formed from gaseous ions (cations and anions).

Lattice energy is the energy required to break one mole of ionic crystal into its constituent gaseous ions.

NaCl

Born Lande Equation

The lattice energy of an ionic crystal is determined by the coulombic interaction between all its ions viz., attractive forces acting between the ions of opposite charges and repulsive forces which result from the interpenetration of their electron clouds.

When the cations and anions approach each other, the only force acting between them is the attractive forces which is directly proportional to the product of charges carried by the cation and anion and inversely proportional to the distance of their separation. Thus the attractive force (or potential energy) is given by

$$(PE)_{attraction} = \frac{(Z_+e)(-Z_-e)}{r} = -\frac{Z_+Z_-e^2}{r} \qquad ...(1)$$

Z_+ and Z_- are charges on cations and anions respectively.

e is the charge on an electron.

r is the interionic distance.

When the inter-ionic distance becomes small enough for the ions to touch, they begin to repel each other. This repulsion originates from the mutual repulsion of the electron clouds on the two ions. The repulsive forces increase rapidly as r decreases. The repulsive force (repulsion energy) is given by

$$(PE)_{repulsion} = \frac{be^2}{r^n} \qquad ...(2)$$

The equation is called Born equation.

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Where b and n are repulsion coefficient and born exponent respectively.

The total energy holding the ions together is the sum of attractive and repulsive forces

$$(PE)_{total} = -\frac{Z_+Z_-e^2}{r} + \frac{be^2}{r^n} \qquad ...(3)$$

In an ionic crystal the force of any one ion will be determined not only by the oppositely charged ions directly surrounding it but also by the other ions (both positive and negative ions) at greater distance. Thus in an ionic crystal not only two separate ions are to be considered but the whole crystal must be considered. In order to consider the forces due to all ions, imagine an ionic crystal $M^{Z+}X^{Z-}$ having NaCl structure in which ions have net charges euqal to Z_+e and $-Z_-e$.

Let us calculate the potential energy at the site of M^{Z+} ion due to all other ions surrounding it.

In a crystal of NaCl type, the potential energy at M^{Z+} ion results from:

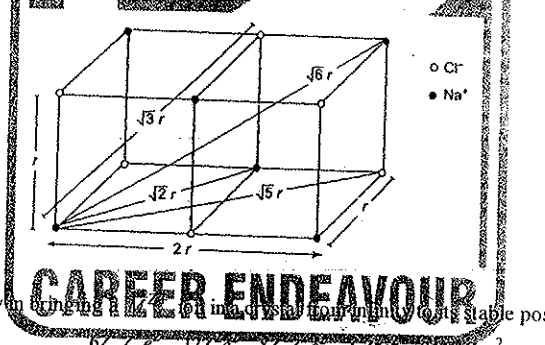
(a) Six nearest X^{Z-} ions at distance r or $\sqrt{1}\,r$.

(b) Twelve next nearest M^{Z+} ions at a distance $\sqrt{2}\,r$.

(c) Eight next nearest X^{Z-} ions at distance $\sqrt{3}\,r$.

(d) Six next nearest M^{Z+} ions at distance $\sqrt{4}\,r$.

(e) Twenty four next nearest X^{Z-} ions at distance $\sqrt{5}\,r$.



Potental energy in bringing the ion in crystal from infinity to its stable position is given by

$$(P.E)_{r} = -\frac{6Z_+Z_-e^2}{r} + \frac{12Z_+e^2}{\sqrt{2}r} - \frac{8Z_+Z_-e^2}{\sqrt{3}r} + \frac{6Z_+e^2}{2r} - \frac{24Z_+Z_-e^2}{\sqrt{5}r} + ...$$

$$= -\frac{Z_+Z_-e^2}{r}\left[6 - \frac{12}{\sqrt{2}}\frac{Z_+}{Z_-} + \frac{8}{\sqrt{3}} - \frac{6}{2}\frac{Z_+}{Z_-} + \frac{24}{\sqrt{5}} .....\right]$$

Since the ratio $\frac{Z_+}{Z_-}$ is constant for a particular crystal (e.g., 1 for NaCl, 2 for CaF_2 etc.). Thus the sum of all the terms is constant. This constant called the Madelung constant (A). The value of this constant depends upon geometry of the crystal and remains independent of the value of Z_+, Z_- and r.

$$(PE)_{M^{Z+}} = -\frac{Z_+Z_-e^2}{r} \times A \qquad ...(4)$$

The same procedure may be used to calculate the potential energy of X^{Z-} ion with all other ions surrounding it.

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$$(PE)_{X^{Z-}} = -\frac{Z_+ Z_- e^2 A}{r} \quad \ldots(5)$$

The total attractive energy is then given by the half of the sum of $(PE)_{M^{Z+}}$ and $(PE)_{M^{Z-}}$.

$$(PE)_{attraction} = -\frac{Z_+ Z_- e^2}{r} \times A \quad \ldots(6)$$

Born suggested that the repulsive forces increases as r decreases and hence nearest neighbours are to be considered. Since each M^{Z+} ion is surrounded immediately by six X^{Z-} ions. Thus repulsive force is given by

$$(PE)_{repulsion} = \frac{6be^2}{r^n} = \frac{Be^2}{r^n} \quad \ldots(7)$$

Where B is born constant and it depends upon the number of nearest neighbours. n is born expont and it depends upon the electronic configeuration of the ion.

The total energy holding the crystal together is the lattice energy (U). That is the sum of the attractive and repulsive forces

$$\ldots(8)$$

The equilibrium distance between ions is determined by the balance between the attractive and repulsive forces. At equilibrium, the equilibrium distance $r = r_0$

and

$$\frac{dU}{dr_0} = \frac{A Z_+ Z_- e^2}{r_0^2} - \frac{n Be^2}{r_0^{n+1}}$$

or

$$\frac{n Be^2}{r_0^{n+1}} = \frac{A Z_+ Z_- e^2}{r_0^2}$$

or $$\ldots(9)$$

Now substituting equation (9) in equation (8)

$$U = -\frac{A Z_+ Z_- e^2}{r_0} + \frac{A Z_+ Z_- e^2}{n} \cdot \frac{1}{r_0}$$

$$= -\frac{A Z_+ Z_- e^2}{r_0} + \frac{A Z_+ Z_- e^2}{n r_0}$$

$$\boxed{U = -\frac{A Z_+ Z_- e^2}{r_0}\left[1 - \frac{1}{n}\right]}$$

This equation is called the Born-Lande equation.

For one mole of the crystal, $U = -\frac{N_0 A Z_+ Z_- e^2}{r_0}\left[1 - \frac{1}{n}\right]$

Consequences of Born-Lande Equation:

(1) The lattice energy varies directly as the product of the charges on ions of the ionic crystal.

e.g., $\xrightarrow[\text{Increasing order of lattice energy}]{LiF < CaF_2 < MgO}$

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(2) Lattice energy varies inversely as the interionic distance r_0.

$$\xrightarrow[\text{Decreasing order of U}]{LiF > LiCl > LiBr > LeI}$$

(3) Crystals with a high lattice energy usually melt at high temperature and are very hard.

Solution (or Hydration) Energy

When a compound is dissolved in a solvent (say water), energy is released. This energy is called solvation energy or hydration energy.

Solubility of Ionic Compounds

If lattice energy of an ionic solid is smaller than the solvation energy (or hydration energy), the ionic solid will dissolve in the solvent (say water). If lattice energy of an ionic solid is greater than the solvation energy, the ionic solid will not dissolve in the solvent (water).

Solvation energy > Lattice energy (Solid dissolve in solvent)

Solvation energy < Lattice energy (Solid will not dissolve in solvent)

Experimental Determination of Lattice Energy (Born-Haber Cycle)

The energy terms involved in building a crystal lattice such as sodium chloride may be taken in steps. The elements in their standard state are first converted to gaseous atoms, and then to ions, and finally packed into the crystal lattice.

The enthalpies of sublimation and dissociation and the ionization energy are positive since energy is supplied to the system. The electron affinity and lattice energy are negative since energy is evolved in these processes.

According to Hess's law the overall energy change in a process depends only on the energy of the initial and final states and not on the route taken. The enthalpy of formation of ΔH_f is the algebraic sum of the terms going around the cycle.

By using known crystal structures, it was possible to calculate the lattice energy, and hence values were obtained for the electron affinity.

$$\Delta H_f = \Delta H_s + I_1 + \frac{1}{2} H_{diss} + E + U$$

For NaCl

hence $E = -348.6$ kJ mol^{-1}

Problem 1. Calculate the lattice energy of NaCl crystal from the following data by the use of Born-Haber cycle.

Sublimation energy (S) = 108.7 kJ mol^{-1}

Dissociation energy for Cl_2 (D) = 22.59 kJ mol^{-1}

Ionization energy for Na(g) (I) = 489.5 kJ mol^{-1}

Electron affinity for Cl(g) E = – 351.4 kJ mol^{-1}

Heat of formation of NaCl (ΔH_f) = – 414.2 kJ mol^{-1}

Solution: Now substituting these values in expression.

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$$U_0 = (-414.2) - (+108.7) - \frac{1}{2}(225.9) - (+489.5) - (-315.4)$$
$$= -414.2 - 108.7 - 112.9 - 489.5 + 351.4$$
$$= -773.9 \text{ kJ mol}^{-1}$$

The lattice energy of NaCl crystal is – 773.9 kJ mol^{-1}.

Problem 2. Calculate the heat of formation (ΔH_f) of KF from its elements from the following data by the use of Born-Haber cycle.

Sublimation energy of potassium (S) = 87.8 kJ mol^{-1}
Dissociation energy for F_2 (D) = 158.9 kJ mol^{-1}
Ionization energy for K(g) (I) = 414.2 kJ mol^{-1}
Electron affinity for F(g) E = – 334.7 kJ mol^{-1}
Lattice energy of KF(U_0) = – 807.5 kJ mol^{-1}

Solution : Now substituting the value in expression

$$\Delta H_f = S + \frac{1}{2}D + I + E + U_0$$
$$= 87.8 + \frac{1}{2}(158.9) + 414.2 + (-334.7) + (-807.5)$$
$$= -569.8 \text{ kJ mol}^{-1}$$

This can be represented as: $K(s) + \frac{1}{2}F_2(g) \longrightarrow KF(s)$ $\Delta H_f = -569.8$ kJ mol^{-1}

Problem 3. Calculate the heat of formation (ΔH_f) of MgF_2 from its elements using the Born-Haber cycle. This example has been taken with an aim to draw your attention to the following points:

(i) The ionization energy (given below) $I(Mg^{2+})$ refers to ΔH for the following reaction:

$$Mg^+(g) \longrightarrow Mg^{2+}(g) + e$$

It is in fact, the sum of first and second ionization energies of Mg.

(ii) The bond dissociation energy of F_2 is not halved but taken as D because two F atoms are used up in the formation of MgF_2.

$$F_2 \longrightarrow 2F(g)$$

(iii) The electron affinity E is taken as twice, i.e., 2E, because two F atoms are converted to two F^- for the formation of MgF_2.

$$F(g) + e \longrightarrow F^-(g)$$

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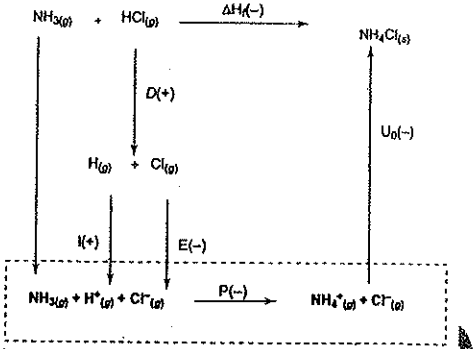
The thermochemical data are as follows:

Sublimation energy of magnesium (S) = 146.4 kJ mol^{-1}
Dissociation energy of F_2 (D) = 158.9 kJ mol^{-1}
Ionization energy for Mg(g) I(Mg^{2+}) = 2184.0 kJ mol^{-1}
Electron affinity for F(g) to (F^-) = – 334.7 kJ mol^{-1}
Lattice energy of MgF_2(U_0) = – 2922.5 kJ mol^{-1}

Solution : Now substituting these values in the expression

$$\Delta H_f = S + D + I + 2E + U_0$$
$$= 146.4 + 158.9 + 2184.0 + 2(-334.7) - 2922.5$$
$$= -1102.6 \text{ kJ mol}^{-1}$$

Proton Affinities : Estimation of proton affinity (P) of ammonia, $NH_3(g) + H^+(g) \longrightarrow NH_4^+(g)$



The values of bond dissociation energy of HCl, ionization energy of H and electron affinity of Cl are 430.9, 1311.6 and –348.5 kJ mol^{-1} respectively. Born-Haber cycle, P can be calculated as follows:

$$\Delta H_f = S + D + I + E + P + U_0$$
$$-144.5 = 217.9 + 430.9 + 1311.6 + (-348.5) + P + (-891.1)$$
$$P = -144.5 + 347.4$$
$$P = -891.1 \text{ kJ mol}^{-1}$$

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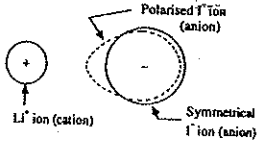
Polarisation of Ions and Fajan's Rules

In the formation of an ionic molecule when two oppositely charged ions (i.e., cation and anion) of the ionic molecule come close to each other, the cation attracts the electron charge cloud of the outermost shell of the anion towards itself and thus the symmetrical shape of the anion gets distorted (*i.e.*, deformed or polarised). The greater the attraction, the greater the distortion in the symmetrical shape of the anion gets deformed by the approach of the cation. This phenomenon is called polarisation (or distortion or deformation) of the anion.



The ability of a cation to polarise an anion is called its *polarising power or polarising ability.*

The tendency of an anion to get polarised by a cation is called its porisability.

Factors Affecting the Magnitude of Polarising Power of a Cation.

Following are important factors which influence the magnitude of the polarising power of cations

1. Magnitude of positive charge on the cation. Higher is the positive charge on the cation, more strongly it attracts the outermost shell electron cloud of the anion towards itself and hence polarises a

given anion more strongly, *i.e.*, with the increase in the magnitude of the positive charge on the cation, the polarising power of the cation also increases.

2. Size of the cation. Smaller is the size of a cation, more strongly it attracts the outer-most shell electron cloud of the anion towards itself and hence greater is its polarising power to polarise a given anion, *i.e.*, with the decrease in the size of a cation, the polarising power of the cation increases.

3. Electronic configurtion of the cation. If we have to compare the polarising power of two cations which have the same positive charge on them and the same or almost same size, then the cation having $ns^2p^6d^{10}$ as its valence-shell configuration will polarise the given anion to a greater extent than the cation having ns^2p^6 as its valence-shell configuration. $ns^2p^6d^{10}$ configuration is called *pseudo-inert gas configuration* while ns^2p^6 configuration is known as *inert gas or noble gas configuration.* Thus a cation containing 18 electrons in its valence-shell has greater polarising power than the cation containing 8 electrons.

Reason. We know that d-electrons shield the nucleus poorly as compared to *s*–and *p*– electrons. Thus *d*-electrons present in an 18-electron cation has poorer shielding of the nucleus than the *s*–and *p*–electrons present in 8-electron cation. Consequently the 18-electron cation would have more greater polarising power than the 8-electron cation.

Examples (a) Although Cu^+ and Na^+ ions have almost the same size (Cu^+ = 96 pm, Na^+ = 95 pm) and the same positive charge (= +1), Cu^+ ion polarises Cl^- ion in CuCl more strongly than Na^+ ion can polarise Cl^- ion in NaCl. Greater polarising power of Cu^+ ion compared to that of Na^+ ion is because of the fact that Cu^+ ion has $3s^2p^6d^{10}$ configuration (18 electrons) while Na^+ ion has $2s^2p^6$ configuration (8 electrons). $3d^{10}$ electrons of Cu^+ ion shield the nuclear charge less effectively than the $2s^2$ and $2p^6$ electrons of Na^+ ion.

(b) Although Hg^{2+} ($5s^2p^6d^{10}$) and Ca^{2+} ($3s^2p^6$) have the same charge and nearly the same size, yet Hg^{2+} ion has more polarising power than Ca^{2+} ion.

Factors Affecting the polarisability of an Anion

Following are the important factors affecting the polarisability of an anion :

1. Magnitude of negative charge on the anion. Higher is the negative charge on the anion, more easily or more strongly its outer-most shell electron cloud is attracted by the cation towards itself and hence the anion is polarised more easily. Thus with the increase in the magnitude of the negative charge on the anion, the polarisability of the anion increases.

2. Size of the anion. Larger is the size of the anion, more easily or more strongly its outermost shell electron cloud is attracted by the cation towards itself and hence greater is the polarisability of the anion *i.e.*, with increase in the size of the anion, the polarisability of the anion also increase.

Example Let us consider the hydrides of halogens namely HF, HCl, HBr and HI. Since the size of the halide ions increases from F^- to I^- ($F^- < Cl^- < Br^- < I^-$), the polarisability of these ions also increases in the same order.

Fajans' Rules of Covalency

In 1924, Fajans told that there are certain conditions which, if fulfilled by the cation and anion of a given ionic molecule, make the ionic bond partially covalent (polar covalent) or purely covalent. These condition are called Fajans' rules which are given below:

1. The cation should have high positive charge on it. Higher is the positive charge on the cation in a given ionic molecule, higher will be its polarising power and hence greater will be the magnitude of covalent character produced in the ionic bond.

2. The cation should be small in size. Smaller is the cation in its size, greater is its polarising power and hence greater is the amount of covalent character produced in the ionic molecule.

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3. The cation should have $ns^2p^6d^{10}$ configuration. A cation having $ns^2p^6d^{10}$ configuration has greater polarising power than the cation having ns^2p^6 configuration. Greater polarising power produces covalent character in the ionic bond. Thus CuCl is covalent while NaCl is ionic. The covalent character of CuCl is because of the fact that Cu^+ ion which has $3s^2p^6d^{10}$ configuration polarises Cl^- ion to a greater extent than Na^+ ($2s^2p^6$) polarises Cl^- ion in NaCl.

4. The anion should have high negative charge on it. Greater is the magnitude of negative charge on the anion, more strongly it gets polarised by a given cation and hence the ionic bond gains covalent character. Thus higher is negative charge on the anion, greater is the magnitude of the covalent character produced in the ionic bond.

5. The anion should be large in size. Larger is the size of the anion, more strongly it is polarised by a given cation and consequently the covalent character increases.

Applications of Fajans' Rules

With the help of Fajans' rules a number of properties like covalent/ionic character, melting points, solubility etc. of the compounds can be explained.

1. Halides having cations of different elements with different positive charge on them. Let us consider NaCl, $MgCl_2$ and $AlCl_3$. In these chlorides, since the number of positive charge on the cation increases from +1 (in NaCl) to +3 (in $AlCl_3$), the polarising power of these cations to polarise Cl^- ion increases as $Na^+ < Mg^{2+} < Al^{3+}$. With the increase in the polarising power of the cations, the covalent character in the given chlorides also increases in the same order ($NaCl < MgCl_2 < AlCl_3$). $AlCl_3$ is essentially covalent in character. It is due to the increasing order of the covalent character that the melting points of these chlorides decrease as $NaCl > MgCl_2 > AlCl_3$ (NaCl = 800°C, $MgCl_2$ = 712°C, $AlCl_3$ = sublimes at 180°C).

2. Halides having cations of the same element with different positive charge on them. If a given main group element forms two chlorides, the chloride of the element with higher positive charge is covalent while that of the element with lower positive charge is ionic.

In order to explain the variation in boiling, solubility and melting point, let us consider $SnCl_4$ — $SnCl_2$ pair as an example. Sn^{4+} ion has higher positive charge and is smaller in size than Sn^{2+} ion, Sn^{4+} ion polarises Cl^- ion in $SnCl_4$ molecule more strongly than Sn^{2+} ion polarises Cl^- in $SnCl_2$ molecule and hence $SnCl_4$ is more covalent than $SnCl_2$. The covalent character of $SnCl_4$ is supported by the fact that it is a colourless liquid which is soluble in C_6H_6 and is a non-conductor of electricity. The ionic character of $SnCl_2$ is shown by its being a solid which is soluble in H_2O. Being covalent, $SnCl_4$ has lower melting point than $SnCl_2$ ($SnCl_4$ = –33°C, $SnCl_2$ = 246°C).

3. Halides having cations of different elements with the same positive charge on them but with different size. (a) *LiCl, NaCl, KCl, RbCl, CsCl.* Lithium metal gives largely covalent compounds, especially halides, while the other alkali metals form largely ionic halides. With the successive increase in the size of M^+ cation (all the cations have the same positive charge on them) from Li^+ to Cs^+, the polarising power of these cations to polarise Cl^- ion decreases in the same direction and hence the covalent character of the chlorides of alkali metals also decreases from LiCl to CsCl (LiCl > NaCl > KCl > RbCl > CsCl). Thus LiCl has the maximum covalent character; while other chlorides are less covalent (*i.e.*, more ionic). Being the most covalent, LiCl has the lowest melting point of all the chlorides (LiCl = 613°C, NaCl = 800°C, KCl = 776°C, RbCl = 715°C, CsCl = 625°C). Now the melting points of other chlorides should increase as NaCl < KCl < RbCl < CsCl. The melting points, however, decrease from NaCl to CsCl. This deccease is due to the successive decrease in the lattice energy values from NaCl to CsCl. Thus we see that the concept of polarisation (Fajans' rules) is not able to explain the variation in the melting points of the chlorides of alkali metals. Being the most covalent, LiCl is insoluble in H_2O but soluble in organic solvents (*e.g.* alcohol and pyridine). On the

othe hand, other chlorides, being less covalent, (*i.e.*, more ionic) are insoluble in organic solvents. NaCl, being ionic, is soluble in water.

(b) *$BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$* and *$BaCl_2$*. Beryllium gives largely covalent compounds, especially halides, while other alkaline earth metals form largely ionic halides. Due the successive increase in the size of M^{+2} cations from Be^{+2} to Ba^{+2} on moving down the group, the covalent character of MCl_2 molecules decreases in the same direction ($BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$). Thus $BeCl_2$ has the maximum covalent character and other chlorides are less covalent (i.e., more ionic). This order is also supported by the fact that the melting points of these chlorides increase in the same direction ($BeCl_2 = 405°C$, $MgCl_2 = 712°C$, $CaCl_2 = 772°C$, $SrCl_2 = 872°C$, $BaCl_2 = 960°C$).

4. Halides of coinage metals and the corresponding halides of alkali metals. Halides of coinage metals are covalent, have lower melting points and are insoluble in water. On the other hand the corresponding halides of alkali metals (whose positive charge and the size is the same as those of coinage metals), have higher melting points and are soluble in water.

Why the halides of coinage metals are covalent and those of alkali metals are ionic can be explained by considering CuCl and NaCl pair as an example. Since Cu^+ ion has $1s^2 2s^2 p^6 d^{10}$ configuration (pseudo-inert gas configuration) and Na^+ ion has $1s^2 2s^2 p^6$ configuration (inert gas configuration), Cu^+ ion polarises Cl^- ion in CuCl more strongly than Na^+ ion polarises the same anion in NaCl. Due to greater extent to which Cl^- ion gets polarised by Cu^+ ion, CuCl becomes covalent and NaCl is ionic. Being covalent, CuCl has lower melting point than NaCl and is insoluble in water while NaCl (which is ionic) is soluble.

5. Compounds having anions of different elements with different negative charge on them. Here we shall consider the variation in covalent character in the ionic bond in the molecules namely CH_4 (C = – 4), NH_3 (N = – 3), H_2O (O = – 2) and HF (F = –1). In all these molecules H^+ acts as a cation. With the decrease in the magnitude of negative charge on the anion from C^{-4} (in CH_4) to -1 (in HF), the case with which the anion gets polarised by the cation (H^+) decreases from C^{-4} to F^- with the decrease of polarisation the covalent character in the ionic bond in the given molecules also decreases, *i. e.*, the covalent character in the order $CH_4 > NH_3 > H_2O > HF$.

6. Halides of a given element.

(*i*) *HF, HCl HBr and HI.* These are the halides of hydrogen. As we go down the group from F^- to I^- ion, the size of these anions (these anions have the same negative charge on them) increases ($F^- < Cl^- < Br^- < I^-$) and hence the extent to which these anions get polarised by H^+ ion also increases in the same direction. With the increase in the polarisability of the halide ions from F^- to I^-, the covalent character of H—X bond or HX molecules also increases in the same direction. Thus HF is the least covalent (maximum ionic character) and HI is the most covalent (minimum ionic character).

(*ii*) *LiF, LiCl, LiBr, LiI.* As we go down the group from F^- ion to I^- ion, the size of these anions (these anions have the same negative charge on them) increases ($F^- < Cl^- < Br^- < I^-$) and hence the extent to which these anions get polarised by Li^+ ion also increases in the same direction ($F^- < Cl^- < Br^- < I^-$). With the increase in the polarisability of the halide ions from F^- ion to I^- ion, the covalent character of the halides also increases in the same direction, i.e., the covalent character of the halides increases as LiF < LiCl < LiBr < LiI, showing that LiF has the least covalent character (*i.e.*, maximum ionic character) and LiI has the maximum covalent character (*i.e.*, least ionic character). Due to the successive increase in the covalent character on proceeding from LiF to LiI, the melting points of these halides show the expected decrease from LiF to LiI (LiF = 870°C, LiCl = 613°C, LiBr = 547°C, LiI = 446°C). Being the least covalent (most ionic) in the series, LiF should be soluble in H_2O and LiI which has the maximum covalent character should be insoluble in H_2O. But the fact is that LiF due to its highest value of lattice energy is insoluble and LiI which has the minimum value of lattice energy is soluble.

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7. Sulphides and oxides of a given metal. Let us consider M_2O and M_2S molecules which are oxide and sulphide of a given monovalent metal cation M^+. Since S^{-2} ion is larger in size than O^{-2} ion, S^{-2} ion gets polarised by M^+ cation to a greater extent as compared to O^{-2} ion by the same cation. Thus M_2S is more covalent than M_2O ($M_2S > M_2O$). Being more covalent, M_2S is less soluble in H_2O than M_2O. In general the sulphides are less soluble in water than the oxides of the same metal. Sulphides being covalent, are soluble in orgainc solvents like alcohol.

8. Hydrides of the elements of groups 15 and 16. Here we shall consider the hydrides namely NH_3, PH_3, AsH_3, SbH_3, BiH_3 (group VA) and H_2O, H_2S, H_2Se and H_2Te (group VIA).

(*i*) *NH_3, PH_3, AsH_3, SbH_3* and *BiH_3*. Due to the successive increase in the size of negatively charged A^{3-} ion (A = N, P, As, Sb and Bi) from N to Bi, the covalent character of the given hydrides increases in the order from NH_3 to BiH_3 ($NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$). This order shows that NH_3 is the least covalent and BiH_3 is the most covalent.

(*ii*) *H_2O, H_2S, H_2Se* and *H_2Te*. We can explain that the covalent character of the given hydrides increases as we move down the group (O to Te) (as explained above in the case of MH_3 hydrides). Thus H_2O is the least covalent and H_2Te is the most so. Being least covalent H_2O is the most stable and hence dissociates only at a high temperature (=2000°C) while H_2Te, being the most covalent is extremely unstable dissociates even at ordinary temperature.

9. Decomposition temperature of metallic carbonates. When a metallic carbonate undergoes decomposition, its CO_3^{2-} ion gets split into CO_2 and O^{2-} ion. Thus the decomposition of a metallic carbonate gives CO_2 and metallic oxide, e.g.

$$MCO_3 \xrightarrow{\Delta} MO + CO_2$$

The temperature at which a given carbonate gets decomposed depends on the polarising power of the cation. The cation with greater polarising power will distort the electron cloud of the neighbouring O-atom of CO_3^{2-} ion very effectively and hence CO_3^{2-} ion would get split into CO_2 and O^{2-} more easily, *i.e.*, the decomposition temperature of a metallic carbonate having the cation with **greater** polarising power will take place at a lower temperature.

(a) *Decomposition of Alkaline Earth Metal Carbonates.* We know that the size of M^{2+} ions (M^{2+} = Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) increases as we move down the group. With the increase in the size of M^{2+} ions, the polarising power of M^{2+} ions decreases down the group and hence the temperature at which MCO_3 molecule gets decomposed into MO and CO_2 increases. Thus $BeCO_3$ decomposes at the lowest temperature while $BaCO_3$ decomposes at the highest temperature [Decomposition temperatures (in °C) are given as $BeCO_3 = 100$, $MgCO_3 = 400$, $CaCO_3 = 900$, $SrCO_3 = 1290$, $BaCO_3 = 1360$). Due to the successive increase in the decomposition temperatures, the thermal stability of these molecules increases as $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$.

10. Variation of the acidic, amphoteric and basic character of the oxides and hydroxides of the elements of group 13. All the elements of group 13 form sesquioxides of the general formula, M_2O_3. Examples are B_2O_3, Al_2O_3, Ga_2O_3, In_2O_3 and Tl_2O_3. These elements also form trihydroxides of $M(OH)_3$ type. The oxides may be considered to have been obtained by the dehydration of $M(OH)_3$ molecules

$$2M(OH)_3 \rightarrow M_2O_3 + 3H_2O$$

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It has been found that, on moving down the group, there is a gradual change from acidic to amphoteric and then to basic character of the oxides and hydroxides. Thus:

$$\underbrace{B_2O_3 \text{ and } B(OH)_3}_{\text{Weakly acidic}} \quad \underbrace{Al_2O_3,\ Al(OH)_3,\ Ga_2O_3,\ Ga(OH)_3}_{\text{Amphoeric}} \quad \underbrace{In_2O_3,\ In(OH)_3,\ Tl_2O_3,\ Tl(OH)_3}_{\text{Basic}}$$

Being acidic, B_2O_3 and $B(OH)_3$ both dissolve in alkalies only. Since Al_2O_3 , $Al(OH)_3$, Ga_2O_3 and $Ga(OH)_3$ are amphoteric, they dissolve both in acids and alkalies. In_2O_3, $In(OH)_3$, Tl_2O_3 and $Tl(OH)_3$, being basic, dissolve in acids only.

Explanation of the variation. The change from acidic to amphoteric and then to basic character can be explained on the basis of the polarising power of M^{3+} ions ($M^{3+} = B^{3+}$, Al^{3+}, Ga^{3+}, $In^{3+}$and Tl^{3+}). Of all the trivalent cations, B^{3+} ion, being the smallest in size, has the highest positive charge density (charge/size) and hence highest polarising power. When $B(OH)_3$ is placed in water, O-atom of H_2O molecule gets coordinated with B-atom of $B(OH)_3$ molecule and thus a hydrated species, $\overset{H}{H}>O\longrightarrow B(OH)_3$ is formed. In this hydrated species, B^{3+} ion, due to its high polarising power, attracts the electrons of the coordinated O-atom towards itself. Coordinated O-atom, in turn, pulls the σ-electron pair of O—H bond in H_2O molecule towards itself sufficiently strongly to rupture the O—H bond. The rupture of O—H bond makes H^+ ions available. The acids thus obtained make the aqueous solution of $B(OH)_3$ weakly acidic. Since $B(OH)_3$ in water acts as a weak acid.

$$H_2O + B(OH)_3 \longrightarrow B(OH)_3 \longrightarrow [B(OH)_3 \cdot OH_2]^- + H^+$$

It is due to the acidic nature of $B(OH)_3$ that it reacts with NaOH solution to produce sodium meta borate, $Na^+BO_2^-.2H_2O$

$$B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$$

$$H_3O^+ + NaOH \longrightarrow Na^+ + 2H_2O$$

$$B(OH)_3 + NaOH \longrightarrow Na^+[B(OH)_4]^- + H_2O$$

$$Na^+[B(OH)_4]^- \text{ or } Na^+BO_2^- + 2H_2O$$

Since the size of M^{3+} ions increases as we move down the group from B^{3+} to Tl^{3+}, the polarising power of the ions decreases. As a consequence, since the polarising power of Al^{3+} and Ga^{3+} ions is less than that of B^{3+} ion, the capacity of these ions to rupture O—H bond present in in $\overset{H}{H}>O\longrightarrow Al(OH)_3$ and $\overset{H}{H}>O\longrightarrow Ga(OH)_3$ to produce H^+ ions is relatively small and hence $Al(OH)_3$ and $Ga(OH)_3$ both, instead of being acidic, are amphoteric. Since In^{3+} and Tl^{3+} ions are even larger than B^{3+}, Al^{3+} and Ga^{3+} ions, their polarising power is so small they cannot rupture O—H bond in $\overset{H}{H}>O\longrightarrow In(OH)_3$ and $\overset{H}{H}>O\longrightarrow Tl(OH)_3$ to produce H^+ ions. As a matter of fact, $In(OH)_3$ and $Tl(OH)_3$ undergo disproportionation in water to give OH^- ions which make the solution basic.

$$\overset{H}{H}>O + In(OH)_3 \longrightarrow \left[\overset{H}{H}>O\longrightarrow In(OH)_3\right]\longrightarrow\left[\overset{H}{H}>O\longrightarrow In(OH)_2\right]^+ + OH^- \text{ and so on.}$$

$$\overset{H}{H}>O + Tl(OH)_3 \longrightarrow \left[\overset{H}{H}>O\longrightarrow Tl(OH)_3\right]\longrightarrow\left[\overset{H}{H}>O\longrightarrow Tl(OH)_2\right]^+ + OH^- \text{ and so on.}$$

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Atomic Radii

Atomic radius is defined *as the distance between the centre of the nucleus to the outermost shell electrons.* However, it is not possible to determine 'the exact radius of an atom due to the following reasons

(i) It is not possible to locate the exact position of electrons in an atom as an orbital has no sharp boundry.

(ii) It is not possible to isolate an individual atom for its size determination.

(iii) If we take a group of atoms, the probability distribution of electrons in atom is influenced by the presence of neigbouring atoms. Therefore, the size of an atom may change in going from one environment to another.

But it is still possible to know the approximate radii of atoms by determining the distance between the atoms in the molecules. These measurements are carried out by X-ray diffraction, electron diffraction, infra red spectroscopy or nuclear magnetic resonance.

Depending upon the types of bonding, atomic radii may be called as *covalent radius, crystal radius, van der Waals radius, metallic radius.* Let us define them one by one.

(a) **Covalent** Radius is defined *as one half of the internuclear distance between the centres of nuclei of two similar atoms bonded together in a molecule by a single covalent bond.* Thus,

$$r_{covalent} = \frac{\text{[Internuclear distance between two bonded atoms]}}{2}$$

For **example,** internuclear distance between two hydrogen atoms in a hydrogen molecule is 0.74Å. **Therefore,** covalent radius of hydrogen

$$r_{(H)} = \frac{0.74\text{Å}}{2} = 0.37\text{Å}$$

Note: The term covalent radius is usually used for non-metallic atoms. In general, the terms atomic radius and covalent radius are used synonymously.

Similarly, the covalent radii of fluorine, chlorine, bromine and iodine are 0.64 Å, 0.99 Å and 1.14 Å respectively.

We can also calculate the internuclear distance in **heteronuclear diatomic molecules** by adding their covalent radii. For example, internuclear distance in HBr molecule should be

$$r_{H} + r_{Br}$$

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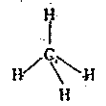
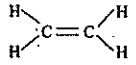
However, covalent radii of elements which do not form diatomic molecules with single covalent bonds are computed by indirect methods. For example, atomic radius of nitrogen is calculated by substracting the atomic radius of carbon from the C—N internuclear distance in CH_3NH_2 (1.47– 0.77 = 0.70Å)

Influence of Hybridization on Atomic Radii

The atomic radius of an atom changes with the type of hybridization as it shown below in the case of carbon atom.

Hybridiza tion	Example	Atomic radius of carbon	percentage of s-characters

sp^3		0.77Å	25
sp^2		0.74Å	33.3
sp	H—C≡C—H	0.70Å	50

From the above table, it is evident that as the percentage of s-character increases, the atomic radius of carbon decreases. *This is because the 2s orbital has smaller radius than 2p orbital.*

(i) The atomic radius decreases from left to right across a period in the periodic table. In a given period, the alkali metal atom is the largest and the halogen atom the smallest.

(ii) The atomic radius increases on descending a group in the periodic table.

(iii) In case of zero group elements, as they are monoatomic in nature, it is impossible to measure their atomic radii. In their case, only Vander Waal's atomic radii are known.

The periodic trends of atomic radii can be easily accounted for in terms of the electronic configuration of these elements.

(i) Variation in a period. The size of atoms decreases from left to right across the period.

How can we explain this decrease in size? This may be explained on the basis of increasing nuclear charge. Since with an increase in the atomic number, the magnitude of **nuclear charge** increases while the corresponding additional electrons enter into the same principal quantum shell. The result is that the increased nuclear charge pulls the electrons more strongly towards the nucleus thereby causing a decrease in the size of the atoms. The decrease in size is the most pronounced when a second '*s*' electron is filled (*i.e.*, in moving from Li to Be), but it is less marked as we fill the *p*-electrons.

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(ii) Variation in a group. The size of elements increases on descending in a group. This may be attributed to the addition of electrons in a new shell at each step. This addition of extra shells of electrons outweighs the effect of increased nuclear charge. This is illustrated by comparing the radii for the elements of group 14.

There is an increase in size from 0.77 to 1.54 Å in going from carbon to lead. In going down the group at each step a new principal shell has been added, thereby causing an expansion in size. It may also be noted from Table that increase in size in a group becomes less pronounced with increase in the atomic number.

Element	Atomic radius (Å)	Nuclear charge	Electronic Configuration
C	0.07	+6	$1s^2 2s^2 2p^2$
Si	1.17	+14	$1s^2 2s^2 2p^6 3s^2 3p^2$

Ge	1.22	+32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Sn	1.41	+50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$
Pb	1.54	+82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$

(b) Crystal Radius (or Metallic Radius). It is defined as *one half of the distance between the nuclei of two adjacent atoms in a metallic crystal.* The term crystal radius is normally used for metallic atoms. Thus

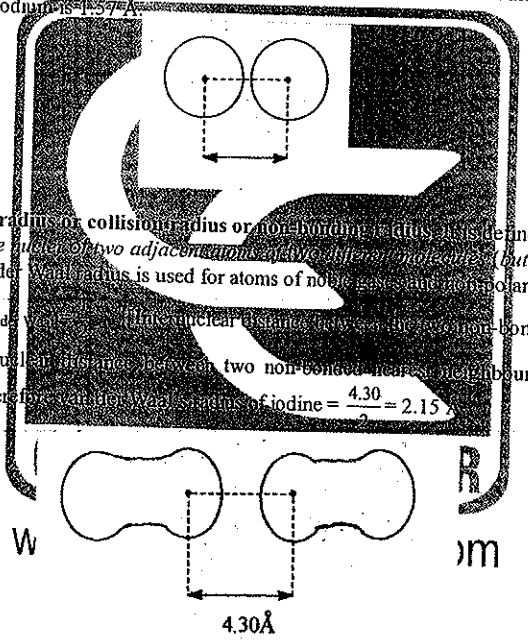
$r_{crystal} = \frac{1}{2}$ **[Internuclear distance between two adjacent same metallic atoms in a crystal]**

The crystal radius or metallic radius indicates the bonding of metallic atoms. For example, the metallic radius of sodium is 1.857 Å. *Since metallic bond is weaker than covalent bond, metallic radius is longer than covalent radius.* For example, the metallic radius of sodium is 1.857 Å while covalent radius of sodium is 1.57 Å.

(c) van der Waal's radius or collision radius or non-bonding radius. It is defined as *one half of the distance between the nuclei of two adjacent atoms of two different molecules (but closest) in the solid state.* The term van der Waal radius is used for atoms of noble gases and non-polar molecules. Thus

$r_{van\ der\ Waal's} = \frac{1}{2}$ [Internuclear distance between two non-bonded closest atoms]

For example, internuclear distance between two non-bonded nearest neighbouring atoms in solid iodine is 4.30 Å. Therefore, van der Waal's radius of iodine $= \frac{4.30}{2} = 2.15$ Å



Since a covalent bond is formed by overlapping of atomic orbitals, therefore, overlap region becomes common to both the combining atoms. Hence, covalent radius is shorter than that of the radius of single atom. On the other hand, van der Waal's radius is calculated from the non-bonded atoms of the nearest neighbouring atoms of the nearest neighbouring molecules. Therefore, no overlapping of the atomic orbitals occurs as shown in figure. Consequently, van der Waal's radii are longer than covalent radii. Thus

van der Waal's radii > Covalent radii

In short, we may conclude that the different radii of the same element follow the order:

Covalent radius < metallic radius < van der Waal's radius

(d) Bragg Slater Radii: Bragg and Slater proposed a new type of radii wherein the effect of bonding between the atoms was not taken into consideration Bragg Slater radii represent radii of inner core of electrons. Hence, these radii are indicative of extent to which the two combining atoms can come closer to each other. These radii decease with increase in nuclear charge.

Ionic Radii

Ionic radius may be defined as the effective distance from the center of the nucleus of the ion upto which it exerts its influence on its electronic cloud. Theoretically, electron cloud may extend up to a large distance. Nevertheless, it is still important to have some value of the ionic radius. For this purpose, the internuclear distance in any ionic compound is determined from X-ray measurement.

Comparison of the ionic radii with corresponding atomic radii.

[A] The radius of the cation is always smaller than that of its parent atom. A cation is formed by loss of one or more electrons from the neutral gaseous atom. This generally causes the removal of the whole of the outermost (valence) shell of electrons.

e.g., Na → Na^+
$1s^2\ 2s^2\ 2p^6\ 3s^1$ → $1s^2\ 2s^2\ 2p^6$

Due to the removal of the valence shell, the number of shells in the cation decreases. As a result, the size of the cation is smaller than the parent atom from which it is formed. Further, due to the removal of electrons from the parent atom, the number of electrons in the cation decreases but its nuclear charge remains the same as that of the atom. As a result, the force of attraction by the nucleus on the electrons increases i.e., effective nuclear charge increases and hence the size of the atom decreases.

The size of a cations is always smaller than that of the corresponding atom due to (i) decrease in the number of shells (ii) increase in the effective nuclear charge resulting in greater force of attraction by the nucleus on the electrons.

Comparative sizes of atoms and their cations

Atom	Li	Na	K	Be	Mg	Al	Mn
Atomic radii (pm)	123	157	203	89	136	143	126
Corresponding cations	Li^+	Na^+	K^+	Be^{2+}	Mg^{2+}	Al^{3+}	Mn^{4+}
Ionic radii (pm)	60	95	133	30	65	50	46

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Variation of ionic (cationic) radii within a group. Like covalent radii of atoms, the ionic radii of cations also increase as we move from top to bottom within a group primarily due to an increase in the number of shells. e.g., the ionic radii of Li^+ is 60 pm, that of Na^+ is 95 pm and that of K^+ is 133 pm.

[B] The radius of the anion is always larger than that of its parent atom. An anion is formed when a neutral gaseous atom gains one or more electrons. This increases the number of electrons in the anion while its nuclear charge remains the same as that on the neutral atom. Since the same nuclear charge now attracts greater number of electrons, therefore, the force of attraction by the nucleus on the electrons of all the shells decreases (i.e., effective nuclear charge decreases). Hence the electron cloud of the atom expands.

The size of an anion is always larger than the corresponding atom mainly because of decrease in the effective nuclear charge i.e. lesser force of attraction by the nucleus on the electrons.

Comparative sizes of atoms and their anions

Atom	F	Cl	Br	I	O	S	N
Atomic radii (pm)	72	99	113	133	74	102	75
Corresponding cations	F^-	Cl^-	Br^-	I^-	O^{2-}	S^{2-}	N^{3-}
Ionic radii (pm)	136	181	196	219	142	184	171

Variation of ionic (anionic) radii with in-group. Like covalent radii, the ionic radii of anions also increase as we move down the group primarily due to all increase in the number of shells. e.g., the ionic radii of F^-, Cl^-, Br^- and I^- ions are 136, 181, 196 and 219 pm respectively.

Isoelectronic Ions or Species: Ions of the different elements which have the same number of electrons but different magnitudes of the nuclear charge are called isoelectronic ions e.g., sulphide ion (S^{2-}), chloride ion (Cl^-) and potassium ion (K^+) are isoelectronic ions because each on of them has 18 electrons but have different nuclear charges i.e., +16, + 17 and +19 respectively. Besides ions, a neutral atom may also have same number of electrons. e.g., besides S^{2-}, Cl^- and K^+ ions, argon (Ar) has also 18 electrons. Therefore, Ar is also isoelectronic with S^{2-}, Cl^- and K^+ ions. In order to convey that these species, the term isoelectronic species is used. Thus, isoelectronic species may be defined as natural or ionic species which have the same number of electrons but different nuclear charges. Thus nitride ion (N^{3-}), oxide ion (O^{2-}), fluoride ion (F^-), sodium ion (Na^+), magnesium ion (Mg^{2+}) and aluminium ion (Al^{3+}) are all isoelectronic species since each one of them contains 10 electrons but different nuclear charges of +7, +8, +9, +10, +11, +12 and +13 respectively.

Variation of ionic size among isoelectronic ions: Within a series of isoelectronic ions, as the nuclear charge increases the force of attraction by the nucleus on the electrons also increases. As a result ionic radii decrease or the ionic radii of isoelectronic ions decrease with the increase in the magnitude of the nuclear charge. e.g., consider the isoelectronic ions: N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}. All these ions have 10 electrons but their nuclear charges vary i.e. these are +7, +8, +9, +11, +12 and +13. Therefore, their ionic radii increase in the order $A^{13+} < Mg^{+} < Na^{+} < F^- < O^{2-} < N^{3-}$.

Isoelectronic species (inert gas, Ne having the same number of electrons like these ions, has the largest radius. Because radius of inert gases is the vander Waal radius which is the largest among the isoelectronic species.

IONIZATION POTENTIAL/ENTHALPY: *The minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom so as to convert it into a gaseous cation is called its ionization enthalpy or energy.*

$$M(g) + \text{energy} \rightarrow M^+(g) + e^-(g)$$

where M(g) and $M^+(g)$ represent the gaseous atom and the resultant gaseous cation respectively.

Successive Ionization Enthalpies. The energy required to remove the most loosely bound electron from the isolated gaseous atom is called its first ionization enthalpy and is denoted by IE_1.

$$M(g) + IE_1 \rightarrow M^+(g) + e^-(g)$$

Similarly, the energies required to remove second and third electrons are called second and third ionization energies respectively, *e.g.*,

$$M^+(g) + IE_2 \rightarrow M^{2+}(g) + e^-(g)$$

$$M^{2+}(g) + IE_3 \rightarrow M^{3+}(g) + e^-(g)$$

where IE_2 and IE_3 are the second and the third ionization enthalpies respectively.

The ionization enthalpies required to remove first, second, third etc. electrons from an isolated gaseous atom are called successive ionization enthalpies.

Exaplanation:

When one electron has been removed from the neutral gaseous atom, the positively charged ion formed has one electron less than the number of protons in the nucleus. As a result, the electrostatic attraction between the nucleus and the remaining electrons in the cation increases, i.e., effective nuclear charge increases. In other words, the positive ion holds its remaining electrons more firmly. Therefore, the energy required to remove another electron from this positively charged ion or second electron from the neutral atom must be higher than the first. Thus, it must be higher than IE_1. Further the removal of two electrons from the neutral atom gives a doubly positively charged ion which will hold its remaining electrons even more tightly. As a result, the energy required to remove third electron from the gaseous atom should be even more than that required for the second electron. i.e., IE_3 must be greater than IE_2. Thus $IE_3 > IE_2 > IE_1$.

Factors Governing the Ionization Enthalpy

[a] Nuclear charge [b] Atomic size [c] Penetration effect of the electrons [d] Screening effect of inner electrons. [e] Effect of arrangement of electrons i.e. effect of exactly half filled or completely filled orbitals

[a] Nuclear charge : The ionization enthalpy increases with increase in nuclear charge. This is due to the fact that with increase in nuclear charge, the electrons in the outer shell are more firmly held by the nucleus and thus more energy is required to pull out an electron from the atom, *e.g.*, the ionization energy increases as we move along a period from left to right due to increased nuclear charge.

[b] Atomic size or Radius : Ionization energy decreases as the atomic size increases. As the distance of the outer electrons from the nucleus increases with increase in atomic radius, the attractive force of the nucleus decreases. Thus, the outer electrons are held less firmly and hence lesser amount of energy is required to knock them out. Thus, ionization enthalpy decreases with increase in atomic size.

[c] Penetration effect of the electrons : Ionization enthalpy increases as the penetration effect of the electrons increases. It is a well known fact that in case of multi-electron atoms, the electrons of the *s*-orbital has the maximum probability of being found near the nucleus and this probability goes on decreasing in case of *p*, *d* and *f*-orbitals of the same shell. In other words, *s*- electrons of any shell are more penetrating towards the nucleus than *p*-electrons of the same shell. Thus, within the same shell, the penetration effect decreases in the order $s > p > d > f$ obviously, if the penetration effect of the electron is more, it will be closer to the nucleus and hence will be held more firmly by the nucleus. Consequently, the ionization enthalpy will be high. In other words, ionization enthalpy increases with the increase in the penetration effect of electrons. Thus, the ionization enthalpy will be more to knock out a *s*-

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electron than *p*-electron of the same shell, which in turn, will be more than that required to remove a *d*-electron and so on.

e.g., *In* Aluminium ($1s^2, 2s^2, 2p^6, 3s^2, 3p^1$), *we have to pull out a p electron from Al to form* Al^+ ion whereas in case of magnesium ($1s^2\ 2s^2\ 2p^6\ 3s^2$) *we have to remove an s-electron of the same energy shell to produce* Mg^+ *ion. since the energy required to remove a p-electrons is lower than that required to knock out a s-electron of the same energy shell, therefore, the first ionization enthalpy of aluminium is lower than that of magnesium. Similarly the first ionization enthalpy of B is lower than that of Be.*

[d] Shielding or Screening effect of the inner shell electrons: As the shielding or the screening effect of the inner electrons increases, the ionization enthalpy decreases. In multi-electron atoms, the electrons in the valence shell experience an attractive force from the nucleus and a repulsive force from the electrons in the inner shells. The overall effect of these two opposing forces is that the attractive force exerted by the nucleus on the valence shell electrons is somewhat reduced by the repulsive force exerted by the electrons present in the inner shells. In other words, the valence shell electrons do not feel the full charge of the nucleus. The actual charge felt by the valence shell electrons is called effective nuclear charge and the repulsive force felt by the valence shell electrons from the electrons present in the inner shells is called the shielding or screening effect.

$$Z_{eff} = \text{Total nuclear charge (Z)} - \text{Screening constant } (\sigma)^*$$

where screening constant (σ)* takes into account the screening effect of the electron present in the inner shells. Obviously greater the number of electrons in the inner shells, larger will be the screening effect. As the screening effect increases, the effective nuclear charge decreases. Consequently, the force of attraction of the nucleus for the valence shell electrons decreases and hence the ionization enthalpy decreases. In other words, an increase in the number of electrons in the inner shells will increase the ionization enthalpy.

[e] Electronic configurations with exactly half-filled or completely filled orbitals: If an atom contains exactly half-filled or completely filled orbitals, then such an arrangement has extra stability. Therefore, the removal of an electron from such an atom requires more energy than expected. e.g.,

(i) Be ($1s^2\ 2s^2$) has higher ionization enthalpy than B ($1s^2\ 2s^2\ 2p^1$). This is because Be has fully filled *s*-orbitals which provide extra stability to the atomic arrangement. Similarly, Mg ($1s^2\ 2s^2\ 2p^6\ 3s^2$) has higher ionization enthalpy than aluminium ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$).

(ii) N ($1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) has higher ionization enthalpy than oxygen ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$). This is because N contains exactly half filled *p*-orbitals. Such an arrangement gives extra stability to the atom. As a result, the removal of electron becomes difficult and hence the ionization enthalpy is high. For similar reasons, ionization enthalpy of P ($1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$) is higher than that of S ($1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$).

(iii) Noble gases have the highest ionization enthalpy in their respective periods. e.g., ionization enthalpy of Ne is more than any other element of the second period. This is due to the fact that ns^2np^6 arrangement that occurs in noble gases is highly stable and hence large amount of energy is needed to remove an electron from this arrangement.

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Variation of ionization enthalppy in the period:
In each period, the minima are found at the alkali metals and the maxima are found at the noble gases. Thus, alkali metals with one electron in the outermost *s*-orbital have lowest ionization enthalpies and hence are highly reactive. In contrast, noble gases with sn^2np^6 configuration have highest ionization enthalpies and hence are chemically inert.

[a] Variation along a period : In general, as we move from left to right in a period, the ionization enthalpy increases with increasing atomic numbers. The observed trends can be easily explained on the basis of increased nuclear charge and smaller atomic radii.

As we move across a period from left to right, the nuclear charge increases and the atomic radius decreases though the principal quantum number of the valence shell remains the same. As a result of increased nuclear charge and simultaneous decrease in atomic radius, the valence electrons are more and more tightly held by the nucleus as we move from left to right in a period. Consequently, more and more energy is needed to remove the electron and hence ionization enthalpies keep on increasing. However, some elements show irregularities in this general trend. These are due to (i) the size of the electron to be removed and (ii) the extra stability of the exactly half-filled and completely filled electronic configurations.

Li and Be : As we move from Li to Be, the ionization enthalpy increases due to increased nuclear charge and smaller atomic radius of Be as compared to that of Li.

Be to B : Although the nuclear charge of B is more than that of Be, yet the ionization enthalpy of B is lower than that of Be.

(i) The outermost electron in B is present in 2*p*-orbital while in Be it is present in 2*s*-orbital since 2*s*-electrons are more penetrating towards the nucleus than 2*p*-electrons, therefore less amount of energy is required to remove a 2*p*-electron than a 2*s*-electron. Consequently, the first ionisation enthalpy of B is lower than that of Be.

(ii) The electronic configuration of B ($1s^2 2s^2 2p^1$) is less stable than that of Be ($1s^2 2s^2$) which has completely filled orbitals. As a result, 2*p*-electron of B is not as strongly attracted by the nucleus as the 2*s*-electron of Be. Consequently, the first ionization enthalpy of B is lower than that of Be.

B to C to N : As we move from B to C to N, the first ionization enthalpy of these elements keeps on increasing due to increasing nuclear charge and decreasing atomic radius.

N to O : The first ionization enthalpy of oxygen is lower than that of N although the nuclear charge of O is higher than of nitrogen. This is due to the following reasons:

(i) The electronic configuration of N is $(1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1)$ in which the 2*p*-orbitals are exactly half filled is more stable than the electronic configuration of O $(1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1)$ in which the *p*-orbitals are neither half-filled nor completely filled. Therefore, it is difficult ot remove an electron from N than from O. As a result, the first ionization enthalpy of N is higher than that of O.

(ii) The removal of an electron O gives an electronic configuration with exactly half-filled 2*p*-subshell, *i.e.*, O^+ $(1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1)$ while this is not so in case of N, i.e., N^+ $(1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0)$. Since the removal of an electron from O gives a more stable

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electronic configuration than that obtained from N, therefore, the first ionization enthalpy of O is lower than that of N.

O to F to Ne : The first ionization enthalpy increases from O to F to Ne because of the increasing nuclear charge. Neon, the noble gas, however, has the highest first ionization enthalpy amongst the elements of the 2nd period because of its *s* (ns^2np^6) electronic configuration.

[b] Variation down a group : The ionization enthalpies keep on decreasing regularly as we move down a group from one elements to the other.

(i) On moving down the group, the atomic size increases gradually due to the addition of one new principal energy shell at each succeeding element. As a result, the distance of the valence electrons from the nucleus increases. Consequently, the force of attraction by the nucleus for the valence electrons decreases and hence the ionization enthalpy should decrease.

(ii) With the addition of new shells, the number of inner electron shells which shield the valence electrons from the nucleus increases. As a result, the shielding or the screening effect increases. Consequently, the force of attraction of the nucleus for the valence electrons further decreases and hence the ionization enthalpy should decrease.

(iii) Nuclear charge increases with increase in atomic number. As a result, the force of attraction by the nucleus for the valence electrons should increase and accordingly the ionization enthalpy should increase.

The combined effect of the increase in the atomic size and the screening effect more than compensates that of the increase in the nuclear charge. Consequently, the valence electrons become less and less tightly held by the nucleus and hence the ionization enthalpies gradually decrease as we move down the group.

ELECTRON AFFINITY : *The electron affinity of an element may be defined as the energy released when a neutral isolated gaseous atom (X) in the ground state accepts an additional electron to form a gaseous negative ion.*

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Evidently, greater the amount of energy released in the above process, higher is the electron affinity of the element. In other words, the electron affinity of an element is a measure of the firmness or strength with which an extra electron is bound to it. Like ionization enthalpy, electron affinity is measured either in electron volts per atom or kJ per mole.

Depending upon the nature of the element, the process of adding an electron to the atom can be either exothermic or endothermic. For majority of the elements, energy is released when an electron is added to the atom. Therefore, for such elements, the electron affinity is negative. e.g., the electron affinity for halogens (i.e., elements of group 17) is highly negative because they can acquire the nearest noble gas configuration by accepting an extra electron. In contrast, noble gases have larger positive electron affinities because the extra electron has to be placed in the next higher principal quantum energy level. Successive Electron Affinities Like second and higher ionization enthalpies, second and higher electron affinities are also possible. However, after the addition of one electron, the atom becomes negatively charged and the second electron is to be added to a negatively charged ion. But the addition of second electron is opposed by electrostatic repulsion and hence the energy has to be supplied for the addition of second electron. Thus the second electron affinity of an element is

positive, e.g., when an electron is added to oxygen atom to form O^- ion, energy is released. But when another electron is added to O^- ion to form O^{2-} ion, energy is absorbed to overcome the strong electrostatic repulsion between the negatively charged O^- ion and the new electron is being added. Thus,

First electron affinity : $O(g) + e^-(g) \rightarrow O^-(g) + \text{Energy}\ (EA_1)$

Second affinity : $O^-(g) + e^-(g) \rightarrow O^{2-}(g) - \text{Energy}\ (EA_2)$

Similarly, the second electron affinity of S is also positive.

Variation in Electron affinity

(i) **Atomic Size.** As the size of the atom increases, the distance between the nucleus and the last shell which receives the incoming electron increases. As a result, the force of attaraction between the nucleus and the incoming electron decreases and hence the electron affinity becomes less negative.

(ii) **Nuclear charge.** As the nuclear charge increases, the force of attraction between the nucleus and the incoming electron increases and hence the electron affinity becomes more negative.

(iii) **Electronic configuration.** Elements having exactly half-filled or completely filled orbitals are very stable. As a result, energy has to be supplied to add an electron. Hence their electron affinities have large positive values.

(iv) **Variation in a group.**

(i) In general, the electron affinity becomes less negative as we move down in a group. As we move down a group, both the atomic size and the nuclear charge increase. But the effect of increase in atomic size is much more pronounced than the nuclear charge. Thus, with increase in atomic size, the attraction of the nucleus for the incoming electron decreases and hence the electron affinity becomes less negative. e.g., The electron affinity of halogens becomes less negative in going from chlorine to bromine to iodine.

(ii) The electron affinities of some of the elements of second period, *i.e.*, O and F are, however less negative than the corresponding elements (i.e., S and Cl) of the third period. This unexpected behaviour is due to the fact that the elements of second period have smallest atomic size amongst the elements in their respective groups. As a result, there are considerable electron-electron repulsions with the 2*p*-subshell and hence the additional electron is not accepted with the same ease as in the case with the remaining elements in the same group. e.g., electron affinity of O (–141 kJ mol^{-1}) and the electron affinity of F (–328 kJ mol^{-1}) is less negative than that of Cl (–349 kJ mol^{-1}). It may be noted that amongst halogens chlorine has the most negative electron affinity.

[b] **Variation in a priod :** Electron affinity becomes more and more negative from left to right in a period. As we move across a period from left to right, the atomic size decreases and the nuclear charge increases. Both these factors tend to increase the attraction by the nucleus for the incoming electron and hence electron affinity, in general, becomes more and more negative in a priod from left to right.

(i) Halogens have the most negative electron affinities. The electron affinities of the halogens (Group 17) elements are the most negative. This is due to the reason that the valence shell electron configuration of the halogens is ns^2np^5 and as such they require one more electron to be a noble gas configuration, *i.e.*, ns^2np^6. As a result, they have a strong tendency to accept an additional electron and hence then electron affinties are highly negative. However, as we move from Cl to I, the electron affinities becomes less and less negative due to a corresponding increase in their atomic radii. In Cl the addition electron enters the 3*p*-subshell; in Br electron enters the 4p-subshell and in I it

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goes to the 5*p*-subshell. As the distance of the nucleus from the subshell which receives the additional electron increses, the force with which it is attracted by the nucleus decreases and hence the electron affinities becomes less negative as we move down the group from Cl to Br to I.

(ii) The electron affinity of F is, however unexpectedly less negative than that of Cl. This is due to its small size of F. As a result of its small size, the electron- electron repulsions in the relatively compact 2*p*-subshell are comparatively large and hence the incoming electron is not accepted with the same ease as in the case with Cl. Consequently, the electron affinity of F is less negative than that of Cl.

(iii) The electron affinity of noble gases is positive. This is due to the fact that the atoms of these elements have completely filled subshells. As a result, there is no room in their valence orbitals and the additional electron has to be placed in an orbital of next higher shell. As a result, energy has to be supplied to add on additional electron. In other words, the electron affinities of noble gases is positive. Further, as we move down the group, the size of the atom increases and hence electron affinities have lower positive values, *e.g.*, electron affinity of Ar (+96) is lower than that of Ne (+116).

(iv) The electron affinity of He is even the lowest of all the noble gases. The reason for this unexpected behaviour is that due to its smallest size, it has much higher tendency to accept an additional electron than any other noble gas.

ELECTRONEGATIVITY *The term electro-negativity has been defined differently by different chemists and each of them has suggested a method of its own to calculate electro-negativities of different elements.*

Pauling's Approach According to Pauling, the tendency (or power) of an element in a molecule to attract the shared pair of electrons towards itself, is called its electro-negativity. He calculated electro-negativities of different elements from thermodynamic data. He considered that in a reaction of the type

$$\frac{1}{2}A-A + \frac{1}{2}B-B \rightarrow A-B$$

the bond dissociation energy of A – B bond is higher than the arithmetic mean of the bond dissociation energies of (A – A) and (B – B) bonds and that their difference (Δ) is related to the difference in the electro-negativities.

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where E_{A-B}, E_{B-B} and E_{B-B} represent the bond dissociation energies of A – B, A – A and B – B bonds respectively and χ_A and χ_B denote the electro-negativities of A and B, Respectively. Thus

$$\Delta = 23(\chi_A - \chi_B)^2$$

or $0.208\sqrt{\Delta} = \chi_A - \chi_B$

Pauling later took the geometric mean instead of the arithmetic mean of E_{A-A} and E_{B-B} and suggested the following empirical correlation:

$$E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2} = \Delta = 30\,(\chi_A - \chi_B)^2$$

or $0.182\sqrt{\Delta} = \chi_A - \chi_B$

In Pauling's equation, the dissociation energies are taken in kcal (and not in kJ) per mole. The extra stability of the A – B bond originates from the polarity developed in it due to the difference in electro-negativities of A and B. The larger the electro-negativity difference, the higher would be the polarity developed and the greater would be, the stability of the A – B bond.

Allred and Rochow's Approach : Allred and Rochow's defined electronegativity as the electrostatic force of attraction exerted by the nucleus of an atom on the valence electrons. Making use of the effective nuclear charge at the periphery of the atom, Z_{eff}, as calculated by Slater's rules they proposed the following empirical relation for calculating the electro-negativity:

$$\chi = 0.359 \times Z_{eff}/r^2 + 0.744$$

where χ is the electro-negativity and r is the covalent radius of the atom in angstrom units. Z_{eff} is calculated according to slater ruler based on screening effect.

i.e., $Z_{eff} = Z - \sigma$

Mulliken's Approach : Mulliken suggested that the average of the ionization energy (IE) and electron affinity (EA) of an atom should be a measure of the electronegativity of the atom. Accordingly, he proposed the following empirical relation for calculating electro-negativity of various elements.

$$\chi = 0.374\left[\frac{IE + EA}{2}\right] - 0.17 = 0.187(IE + EA) + 0.05$$

In this equation, ionization energy as well as electron affinity are in electron volts.

Factors Affecting Electronegativity

(1) Charge on the Atom : An atom which acquires a positive charge, either integral or partial, would tend to attract electrons more strongly than a neutral atom. Thus, a cation will be more electronegative than the parent atom while an anion is more electronegative than its parent atom. Also, the higher the positive oxidation state of an element, the greater would be its electron-attracting power and hence the greater would be its electronegativity. Thus the oxidation state of central chlorine atom is +1 in HClO and +5 in $HClO_3$. Hence, the chlorine atom in $HClO_3$ is more electronegative than in HClO. Accordingly, the release of hydrogen as H^+ ion in $HClO_3$ would be much easier than a similar change in HClO. In other words, $HClO_3$ behave as a stronger acid than HClO.

(2) Hybridisation : We know that *s* electrons are more penetrating than the *p* electrons. Therefore, if an atom has hybrid orbitals with a greater *s* character, the electronic charge in such orbitals would remain closer to the nucleus of that atom. This means that the electro-negativity of the atom would increase with increase in *s* character of its hybrid orbitals. e.g., in methane, the carbon atom involves sp^3 hybridization of its orbitals so that the hybrid orbtials have 25% *s* character. In ethylene, the carbon atom involves sp^2 hybridization of its orbitals and consequently the *s* character of hybrid orbitals increases to 33%. In acetylene, the carbon atom involves sp hybridization of its orbitals and, therefore, the *s* character of hybrid orbitals increases to 50%. Accordingly the electro-negativity of carbon atom increases as we move from CH_4, through C_2H_4 to C_2H_2. Due to greater electro-negativity of carbon atom in ethylene and acetylene, the electron pair of C-H bond is pulled more towards carbon atom thereby facilitating the release of H atom as H^+ ion. Thus, while methane is neutral, ethylene is slightly acidic while acetylene is considerably acidic.

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Similarly, the basicity of amines also varies with the type of the hybridization of the orbitals, the greater would be the electro-negativity, lower would be the electron donating power of the nitrogen atom and hence lower would be the basicity of the amine. e.g., the molecules $R-C \equiv N$, C_5H_5N (pyridine) $C_6H_5NH_2$, involve, respectively, sp, sp^2 and sp^3 hybridisation of the orbitals of the nitrogen atom. Accordingly, the *s* character of the hybrid orbitals of nitrogen atom is 50% in RCN, 33% in pyridine and 25% in aniline. Thus aniline is more basic than pyridine which is more basic than $RC \equiv N$

(3) Effective nuclear charge : The electron attracting power of an atom in a molecule is proportional to the effective nuclear charge, Z_{eff}. Thus any factor which increase Z_{eff} should also increase the electro-negativity of the atom. e.g., Z_{eff} decreases as we go down a group in the periodic table. This is because with increase in atomic number within a group, the atomic size increases. Hence, electro-negativity decreases as we move down a group. Thus, the electro-negativity of the halogens decreases in the order :

$$F (4.0) > Cl (3.0) > Br (2.8) > I (2.5)$$

Z_{eff} increases with decrease in size of the atom and the size of the atom decreases as move along a period from left to right in the periodic table. Accordingly, electronegativities goes on increasing with increase in atomic number as we move along a period. Thus, electronegativities of the element of the second period increases in the order

$$Li (1.0) < Be (1.5) < B (2.0) < C (2.5) < N (3.0) < O (3.5) < F (4.0)$$

Z_{eff} also depends upon the number of inner electrons which screen the outer electron. The larger the number of inner electrons, the greater would be the screening and the lesser would be the effective nuclear charge. Thus electronegativity would decrease with increase in the number of inner electrons in atoms of the elements in the same group. This is an additional reason why the electro-negativity of alkali metals decreases in the order

$$Li (1.0) > Na (0.9) > K (0.8) > Rb (0.8) > Cs (0.7)$$

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INTERMOLECULAR FORCES

The forces between the molecules of a substance are known as intermolecular forces. Such forces exist in all states of matter and are responsible for many physical properties of matter.

Intermolecular forces are weak forces. It usually requires, for example, much less energy to evaporate a liquid than to break the chemical bonds in the molecules of the liquid. The boiling points of substances often reflect the strength of intermolecular forces operating among the molecules. At the boiling point, enough energy must be supplied to overcome the attractive forces among molecules before they can enter into vapour phase. Similarly, the melting point of substances increases with increase in the strength of the intermolecular forces.

Intermolecular forces arise due to the following type of interactions: Dipole-dipole, Ion-dipole, Ion-induced dipole, dipole induced dipole, dispersion forces and Hydrogen bonding. The term 'van der Waals forces' refers to dipole-dipole, dipole-included dipole and dispersion forces. Depending on the phase of the substance, the nature of chemical bonds and the types of element present, more than one type of interaction may contribute to the total attraction between molecules.

DIPOLE-DIPOLE INTERACTIONS

Dipole-dipole interactions depend upon the distance and orientation of the two dipoles. A favourable orientation of the two dipoles results in attractive dipole-dipole interactions.

It exist between molecules having permanent dipoles. The gases like NH_3, SO_2, HF, HCl etc. are the examples of polar molecules. Although polar molecules are neutral, they have permanent dipole moments, i.e., a polar molecule behaves as a dipole. The dipole-dipole ineractions are the electrostatic interactions b/w the positive end of one dipole and negative end of other dipole. Greater is the dipole moment, greater will be the dipole-dipole interaction.

ION-DIPOLE INTERACTIONS

Ion-dipole interactions attract an ion (either a cation or an anion) and a polar molecule to each other. The strength of this interaction depends on the charge and size of the ion and on the magnitude of the dipole moment and size of the polar molecule. The charge density on cations is higher than on anions, therefore, a cation interacts more strongly with dipoles than does an anion having same charge but bigger size. Hydration of different ions is an example of ion-dipole Interaction: In an aqueous NaCl solution, the Na^+ and Cl^- ions are surrounded by water molecules, which have a large dipole moment. When an ionic compound like NaCl dissolves, the water molecules act as a dielectric to keep the ions apart. On the other hand, carbon tetrachloride (CCl_4), a nonpolar molecular lacks the ability to participate in ion-dipole interaction. Therefore, carbon tetrachloride is a poor solvent for ionic compounds, as are most nonpolar liquids.

ION-INDUCED DIPOLE INTERACTIONS AND DIPOLE-INDUCED DIPOLE INTERACTIONS

The attractive interaction between an ion and the induced dipole is called ion-induced dipole interaction, and the attractive interaction between a polar molecule and the induced dipole is called dipole-induced dipole interaction. The likelihood of a dipole moment being induced depends not only on the charge on the ion or the strength of the dipole but also on the polarisability of the atom or molecule, i.e., the ease with which the electron distribution in the atom (or molecule) can be distorted.

DISPERSION FORCES OR LONDON FORCES OR INDUCED DIPOLE-INDUCED DIPOLE INTERACTIONS

Dispersion forces are the attractive forces between atoms in substances such as O_2, N_2 or monoatomic gases such as *He*, *Ar*, etc. These arise as a result of instantaneous dipoles created in these nonpolar molecules or atoms. Let us understand the origin of these forces, say in helium gas, In a helium atom the electrons are moving at some distance from the nucleus. At any instant it is likely that the atom has a dipole moment created by the fleeting momentary displacements of electrons. This dipole moment is called an instantaneous dipole because it lasts for just a fleeting moment. In the next instant the electrons are in different locations and the atom has new instantaneous dipole, and so on. Averaged over time (that is the time it takes to make many instantaneous measurements), however the atom has no dipole moment because the instantaneous dipole all cancel one another. In a collection of *He* atoms, an instantaneous dipole of one *He* atom can induce a dipole in each of its nearest neighbours. At the next moment, a different instantaneous dipole can create temporary dipoles in the Surrounding He atoms. This kind of interaction produce attractive dispersion forces between *He* atoms. At very low temperatures, dispersion forces are strong enough to hold He atoms together, causing the gas to condense. The attraction between nonpolar molecules can be explained similarly.

FACTOR EFFECTING THE VAN DER WAAL'S FORCES

Van der Waal's forces are very weak forces. However, strength of these forces depends on the following factors:

(i) Size of the molecule : van der waal's forces increase as the size of the molecule increases. This is reflected in their boiling points. For example, in case of isomeric pentanes, the boiling points increases as the size of the molecule increases as

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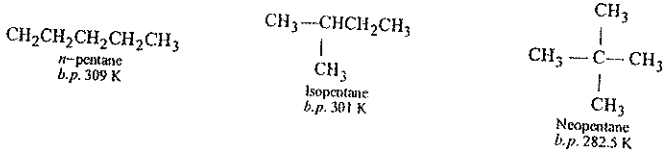

It is due to the fact that larger the size of molecule, larger will be surface area and thus larger will be the value of van der Waal forces.

(ii) Number of electrons present in the molecule: As the number of electrons in the molecule increases, it results in increased probability of distortion of electron clouds and hence greater van der Waal's forces in the molecule. This is reflected in the increases in their boiling points. For example, Xenon having 54 electrons has boiling point 165 K, while helium having 2 electrons has boiling point only 4.2 K.

THE HYDROGEN BOND

Nitrogen, oxygen and fluorine are the three most electronegative elements. When they are attached to a hydrogen atom the electrons are drawn towards the electronegative atom. This H atom attached to nitrogen, oxygen or fluorine is able to interpose itself between two such electronegative atoms bonding them together. This is called hydrogen bond. The essential requirements for an. H-bond are : (i) a hydrogen atom attached to a highly electronegative atom and (ii) a lone pair of electrons on the electronegative atom. The hydrogen bond is written as A–H.....B or A–H.....A, where A and B represent O, N or F: A–H is one molecule or part of the molecule and B is part of another molecule and the dotted line represents the hydrogen bond. The three atoms usually are not in a straight line, but the angle AHB (or AHA) can deviate as much as 30° from linearity. Only the O, N and F atoms all possess at least one lone pair of electrons that can interact with the hydrogen atom in hydrogen bonding. The energy of a hydrogen bond is of the order of 5 kcal/mol. Hydrogen bonds have a powerful effect on the structures and properties of many compounds.

The boiling points of a series of compounds containing elements in the same periodic group normally increase with increasing molar mass. Thus the hydrogen bonded compounds of the elements in Groups 15, 16 and 17 with hydrogen follow this trend. In these series, the lightest compound (NH_3, H_2O and HF) has the highest boiling point, contrary to expectations based on molar mass. The reason is that there is extensive hydrogen bonding between molecules in these compounds. Some unique properties of water, such as its exceptionally high boiling point than of water and the contraction of water when heated between O°C and 4°C can also be explained on the basis of hydrogen bonding.

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Structure & Bonding

1. Calculate the miller indices of the crystal plane which cut through the crystal axes at (2a, 3b, c):

(a) 326 (b) 122 (c) 236 (d) 623

2. For an ionic crystal of the general formula AB and coordination number six, the value of radius ratio will be:

(a) in between 0.41 and 0.22 (b) less than 0.22

(c) greater than 0.73 (d) in between 0.73 and 0:41

3. Orthorhombic crystal system has the following unit all dimensions:

(a) $a = b = c$ & $\alpha = \beta = \nu = 90^0$ (b) $a \neq b \neq c$ & $\alpha = \beta = 90^0$

(c) $a = b \neq c$ & $\alpha = \beta = 90^0$; $\nu = 120^0$ (d) $a \neq b \neq c$ & $\alpha = \beta = \upsilon = 90^0$

4. Madlung constant is often used to deal with:

(a) ionic crysrtals (b) metallic crystals

(c) covalent crystals (d) molecular crystals

5. One 3 – fold axis is found in:

(a) triclinic (b) tetragonal (c) rhombohedral (d) cubic

6. The number of symmetry elements in cubic crystals is:

(a) 14 (b) [illegible] (c) 32 (d) [illegible]

7. Diamond has the number of atoms per unit cell is:

(a) 2 (b) [illegible] (c) 8 (d) [illegible]

8. The arrangement of [illegible] is found to be represented symmetry:

(a) one 4-fold axis (b) one 6-fold axis

(c) one 2-fold axis (d) one 3-fold axis

9. Which of the arrangement has four 3- fold axis of symmetry?

(a) ABABA..... (b) ABCABC..... (c) [illegible] (d) None of the above

10. The stoichiometry ratio in CaF_2 is found to be

(a) 1:2 (b) 2:1 (c) 4:4 (d) 6:3

11. In CaF_2, each F^- ions is surrounded by

(a) 8 Ca^{+2} ions (b) 4 Ca^{+2} ions (c) 2 Ca^{+2} ions (d) 6 Ca^{+2} ions

12. Zinc blends has the coordination number:

(a) 8:8 (b) 4:4 (c) 6:6 (d) 8:4

13. The radius ratio $\frac{r^+}{r^-} = 0.524$ belongs to the co-ordination no.

(a) 8 (b) 4 (c) 6 (d) 12

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14. The example of metal deficiency defect is:

(a) KCl (b) NaCl (c) NiO (d) SiO_2

15. Which of the following has the inverse spind structure?

(a) $Zn_2 TiO_4$ (b) $Fe TiO_3$ (c) $Mg Al_2 O_4$ (d) TiO_2

16. Schottky defects are due to the absence of:

(a) one+ve ion (b) one – ve ion

(c) two + ve ion & one –ve ion (d) one +ve ion & -ve ion

17. Schottky defects lower the density of the crystals but Frenkel defects:

(a) do not change the density (b) increase the density

(c) decrease the density (d) both (b) and (c)

18. Which of the following has the ilmenite structure?

(a) TiO_2 (b) $CaTiO_3$ (c) $FeTiO_3$ (d) $ZnTiO_4$

19. Which of the following has the Perovskite structure?

(a) $FeTiO_3$ (b) $CaTiO_3$ (c) $ZnTiO_4$ (d) $MgAl_2O_4$

20. The electron transform Fe^{+2} to Fe^{+3} causes virtual migration of Fe^{+3} ion, which type of conduction is found?

(a) p-type (b) n-type (c) extrinsic (d) all

21 AgBr and ZnS crystals are the example of the defects respectively:

(a) Frenkel and Schottky (b) Schottky and Frenkel

(c) Frenkel and Frenkel (d) Schottky and Schottky

22. NH_4Cl crystal has the coordination no:

(a) 6:4 (b) [illegible] (c) [illegible] (d) 8:8

23. Which of the following has the F-centre?

(a) metal excess defects (b) metal deficiency defects

(c) Insulator (d) Rectifiers

24. The n-type semi- conductor formed is formed due to:

(a) Metal excess defects (b) Metal deficiency defects

(c) Compton effect (d) Zeeman effect

25. Intrinsic conduction is due to:

(a) Cs (b) Si (c) As (d) In

26. The p-type semi conductor is formed due to:

(a) metal excess defects (b) metal deficiency defects

(c) stark effect (d) kerr effect

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27. Which of the following crystal system has the point gp 'Ci'?

(a) Orthorhombic (b) Monoclinic

(c) Triclinic (d) Cubic

28. NH_4F crystal has the coordination no. is:

(a) 6:6 (b) 8:8 (c) 4:4 (d) 8:4

29. Yellow phosphorus exhibit the geometry:

(a) Monoclinic (b) Cubic (c) Triclinic (d) Tetragonal

30. Red Phosphorous exhibit the geometry:

(a) Rhombohedral (b) Cubic

(c) Monoclinic (d) Tetragonal

31. The correct order of increasing the polarization power of the cations

(a) $AlCl_3 < MgCl_2 < NaCl$ (b) $MgCl_2 < NaCl < AlCl_3$

(c) $NaCl < MgCl_2 < AlCl_3$ (d) $NaCl < AlCl_3 < MgCl_2$

32. Which of the following has the least melting point?

(a) LiI (b) LiF (c) LiBr (d) LiCl

33. The decreasing order of the solubility of the sulphates is

(a) $BeSO_4 > MgSO_4 > CaSO_4$ (b) $CaSO_4 > MgSO_4 > BeSO_4$

(c) $BeSO_4 > CaSO_4 > MgSO_4$ (d) $CaSO_4 > BeSO_4 > MgSO_4$

34. Ice has the geometry of the type of

(a) hexagonal (b) tetragonal (c) triclinic (d) cubic

35. A cubic crystal system has the number of plane of symmetry and number of axis of symmetry respectively:

(a) 14, 9 (b) 13, 9 (c) 9, 13 (d) 9, 14

36. The molecules NO_2 and ClO_2 are respectively:

(a) diamagnetic, paramagnetic (b) paramagnetic, paramagnetic

(c) paramagnetic, diamagnetic (d) diamagnetic, diamagnetic

37. Which of the following has the lowest melting point?

(a) o-nitrophenol (b) m-nitrophenol

(c) p-nitrophenal (d) none

38. Which is paramagnetic and coloured compounds?

(a) $(NH_4)_2$ Ti Cl_6 (b) K_2 Cr_2 O_7

(c) $VOSO_4$ (d) K_3 [Cu (CN) $_4$]

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39. Which of the following is expected to be coloured?

(a) CuF_2 (b) CuCl (c) MgF_2 (d) Ag_2SO_4

40. The metal which forms a coloured chloride is:

(a) Zn (b) Sn (c) Al (d) Cr

41. The correct order of electron affinity of the halogens is:

(a) F < Cl < Br >I (b) F < Cl > Br < I

(c) F < Cl < Br < I (d) F > Cl < Br > I

42. Which of the following has highest ionization energy?

(a) B (b) N (c) O (d) C

43. The highest electron affinity is:

(a) Cl (b) F (c) Br (d) I

44. Which is amphoteric oxide?

(a) MgO (b) SiO_2 (c) P_2O_5 (d) Al_2O_3

45. Which is the inert oxide?

(a) NO (b) NO_2 (c) N_2O (d) N_2O_5

46. The correct order of acidity is:

(a) HClO < $HClO_2$ < $HClO_3$ < $HClO_4$ (b) $HClO_4$ < $HClO_3$ < $HClO_2$ < HClO

(c) HClO < $HClO_4$ < $HClO_2$ < $HClO_3$ (d) $HClO_3$ < $HClO_2$ < HClO < HCl

47. Which of the halides SnX_4 (X = Cl, Br, I) has doubtful existence?

(a) SnI_4 (b) $SnBr_4$ (c) PbI_4 (d) $SnCl_4$

48. The neutral oxide is:

(a) SiO_2 (b) SnO (c) PbO (d) ZnO

49. The no. of microstates for P^2 and d^2 are:

(a) 20 and 252 (b) 252 and 20

(c) 15 and 210 (d) 252 and 210

50. The number of microstates for d^3 and d^7 are:

(a) 120, 120 (b) 210,210

(c) 120,210 (d) 210, 120

51. $H_2C = C = CH_2$ has the point group of:

(a) C_2v (b) D_2h (c) D_2d (d) C_3v

52. The ionic raddi of A^+ and B^- ions are 0.98×10^{-10} and 1.81×10^{-10}m.The co-ordination no. of each ions is:

(a) 8 (b) 4 (c) 6 (d) 0

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53. The least polarized anion is:

(a) $C_2O_4^{-2}$ (b) NO_3^- (c) ClO_4^- (d) SO_4^{-2}

54. The correct order of the O-O bond length in O_2, O_2^{-2} O_3, is:?

(a) $O_2 > O_3 > O_2^{-2}$ (b) $O_2^{-2} > O_3 > O_2$

(c) $O_2 > O_2^{-2} > O_3$ (d) $O_3 > O_2^{-2} > O_2$

55. Which of the following has the highest lattice energy?

(a) KF (b) RbF (c) NaF (d) CsF

56. The number of unshared valence electron pairs in XeF_2 is:

(a) 2 (b) 4 (c) 3 (d) 1

57. The shape and expected hybridization of BrO_3^- and HOCl are:

(a) BrO_3^- pyramidal and sp^3 & HOCl planar sp^2

(b) BrO_3^- pyramidal sp^3 and HOCl angular sp^2

(c) BrO_3^- angular dsp^2 and HOCl linear sp

(d) BrO_3^- trigonal sp^2 and HOCl angular sp^3

58. The splitting of spectral lines when the source is placed in a magnetic field is known as:

(a) Sark effect (b) Compton effect

(c) Shielding effect (d) Zeeman effect

59. The splitting of spectral lines in the presence of an external electric field is:

(a) Stark effect (b) Compton effect

(c) Kerr effect (d) Zeeman effect

60. I_3^- ion is linear having the hybridization:

(a) sp (b) sp^2 (c) sp^3d (d) sp^3

61. The molecule which has zero dipole moment:

(a) H_2O (b) BCl_3 (c) NH_3 (d) SO_2

62. Germanium is an example of a:

(a) n-type semi conductor (b) p-type semiconductor

(c) Insulator (d) intrinsic semiconductor

63. If Indium in small amount of Ge metal we get a:

(a) rectifier (b) insulator

(c) p-type semiconductor (d) none

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64. Due to the formation of Schottky defects, the density of the crystal:

(a) increases slightly (b) decreases slightly

(c) decreases appreciably (d) increases appreciably

65. The ionization potential of hydrogen atom is 13.6 eV, the K.E. of the electron in hydrogen atom is:

(a) 31.6 eV (b) -13.6 eV (b) + 13.6 eV (d) 6.8 eV

66. The wave no. of the light emitted by certain source is 2×10^6 m^{-1}. The wavelength of this light is:

(a) 500nm (b) 500 m (c) 200 nm (d) 200 m

67. Electrostatic forces are:

(a) directional (b) Non-directional

(c) both (a) and (b) (d) None

68. Ion-dipole interaction are:

(a) directional (b) Non-directional

(c) both (a) and (b) (d) None

69. The $[Co(NH_3)_6]^+$ ion is an example of:

(a) dipole-dipole interaction (b) induced dipole interaction

(c) electrostatic ion-dipole interaction (d) all

70. The easily liquefied gases are those which have:

(a) dipole induced interaction (b) non-polar induced interaction

(c) ion-dipole interaction (d) induced dipole interaction

71. Which one of the following gas is easily liquified?

(a) CH_4 (b) H_2 (c) O_2 (d) SO_2

72. Which one of the following interaction has permanent dipole moment?

(a) dipole- dipole interaction (b) dipole induced interaction

(c) induced-induced interaction (d) None

73. London force (F) vary inversely to the distance (r) between the adjacent molecules:

(a) $F\alpha\frac{1}{r^2}$ (b) $F\alpha\frac{1}{r^4}$ (c) $F\alpha\frac{1}{r^6}$ (d) $F\alpha\frac{1}{r^5}$

74. The electrostatic forces of attraction between induced dipoles and original dipoles are known as:

(a) adhesive forces (b) cohesive forces

(c) dispersive forces (d) nuclear forces

75. The bond angle of Cl_2O is:

(a) smaller than that of F_2O (b) smaller than that of H_2O

(c) greater than that of H_2O (d) same as that of F_2O

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76. On the basis of LCAO-MO theory, the magnetic characteristics of N_2 and N_2^+ are:

(a) both paramagnetic (b) both diamagnetic

(c) N_2 paramagnetic and N_2^+ diamagnetic (d) N_2 diamagnetic and N_2^+ paramagnetic

77. In units of $h^2/8ml^2$, the energy difference between levels corresponding to 3 and 2 node eigen functions for a particle of mass m in one dimensional box of length l is:

(a) 7 (b) 3 (c) 5 (d) 1

78. In which of the molecule, the bond order is 1.5?

(a) O_2 (b) O_3 (c) N_2 (d) F_2

79. In which of the ion, the bond order is $1\frac{1}{3}$:

(a) NO_3^- (b) NO_2^- (c) O_2^- (d) NO

80. The correct order of increasing O – O bond length is:

(a) $O_2^{-1} > O_2^{+1} > O_2^{-2}$ (b) $O_2^{-2} > O_2^{-1} > O_2$

(c) $O_2^{+1} < O_2^{-1} < O_2^{-2}$ (d) $O_2^{+1} < O_2^{+2} < O_2^{-1}$

81. The bond order of F_2 is:

(a) 1 (b) 2 (c) 0 (d) 3

82. Which of the molecule has the greatest bond length?

(a) B_2 (b) N_2 (c) O_2 (d) CO

83. The correct increasing order of bond angles is:

(a) $Cl_2O < Br_2O < I_2O$ (b) $I_2O < Cl_2O < Br_2O$

(c) $Br_2O < Cl_2O < I_2O$ (d) $Cl_2O < I_2O < Br_2O$

84. The molecule XeO_2F_2 has the hybridization of:

(a) sp^3 (b) sp^3d^2 (c) sp^3d (d) sp^2

85. The geometry of $XeOF_3^+$ ion is:

(a) T- shaped (b) V-shaped (c) See-saw (d) All

86. Which of the molecule has the see-saw geometry?

(a) XeO_2F_2 (b) XeO_4 (c) XeO_3 (d) XeO_3F_2

87. The hybridization of Ni atom in $[Ni(CN)_4]^{-2}$ is found to be of the type of:

(a) sp^3 (b) sp^2d^2 (c) dsp^2 (d) d

88. In the $Ni(CO)_4$ Carbonyl the Ni atom has the hybridization:

(a) sp^3 (b) SP^3d^2 (c) dsp^2 (d) SP^3d

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89. ψ^2 measures:

(a) The hybrid character of orbitals

(b) The probability of finding an electron in a given region

(c) The energy of the electron in n^{th} orbit

(d) none

90. Assuming that the $CH_3^{\bullet}$ radical is planar, the unpaired electron is in the orbital of:

(a) $2p_x$ (b) $2p_z$ (c) $2p_y$ (d) all

91. The zero point energy is equal to:

(a) kT (b) 1./2 kT (c) hν (d) ½ hν

92. There is no S-S bond in:

(a) $S_2O_7^{-2}$ (b) $S_2O_6^{-2}$ (c) $S_2O_3^{-2}$ (d) $S_2O_8^{-2}$

93. The Balmer series falls in the:

(a) Visible region (b) UV region

(c) IR region (d) Micro-wave region

94. Which of the following series falls in the IR region?

(a) Balmer (b) Paschen (c) Lyman (d) None

95. The zero point energy of a particle in a box is equal to:

(a) $\frac{h^2}{4ma^2}$ (b) $\frac{h^2}{2ma^2}$ (c) $\frac{h^2}{8ma^2}$ (d) $\frac{h^2}{ma^2}$

96. What is the wavelength of the electron in the 3rd Bohr orbit?

(a) $\lambda = (n \times 2 \times 3.14 \times 0.529)$ Å (b) $\lambda = (n \times 2 \times 3.14 \times 0.529)$ Å

(c) $\lambda = (n \times 2 \times \pi \times 0.529)$ Å (d) none

97. Which of the following has the lowest thermal stability?

(a) $CaSO_4$ (b) $MgSO_4$ (c) $BeSO_4$ (d) $BaSO_4$

98. Which is correct among the following?

(a) Bond energy α bond length (b) bond energy = bond length/ 2

(c) bond energy $\alpha \frac{1}{\text{bond length}}$ (d) None

99. The XeO_2F_2 molecule has the no. of lone pair:

(a) 2 (b) 1 (c) 3 (d) 0

100. The radial function depends upon the quantum no's are:

(a) m, l (b) n,l (c) s,l (d) only l

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101. orbital quantum no.'s are:

(a) m, l (b) n,l (c) only m (d) only l

102. The angular function is:

(a) dependent of the distance (b) independent of distance

(c) dependent on the direction (d) both (b) and (c)

103. Schrödinger equation for a particle in one Dimensional box:

(a) $\frac{\partial^2\Psi}{\partial x^2}+\frac{2m}{h}(E-\infty)\Psi=0$ (b) $\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2m}{h^2}(E-V)=0$

(c) $\frac{\partial^2\Psi}{\partial x^2}+\frac{2m}{h}(E-V)\Psi=0$ (d) $\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2m}{h^2}(E-\infty)=0$

104. The eigen functions of a Hermitian operator are [illegible] an orthonormal set i.e. $\int\Psi_n\Psi_m d\tau=0$ [for n≠m]

(a) Normalized (b) Orthogonal

(c) Radial function (d) Non-orthogonality

105. An orthonormal set is normalized if $\int\Psi_n\Psi_m d\tau=$

(a) 0 (b) [illegible] (c) [illegible] (d) always the value

106. The zero point energy of a simple Harmonic oscillator is:

(a) $\left(1+\frac{1}{2}\right)h\upsilon$ (b) [illegible] (c) ½ hυ (d) [illegible]

107. Schrödinger equation for a particle in three-dim[illegible]

(a) $\nabla^2\Psi+\left(\frac{2mE}{h}\right)\Psi=0$ (b) $\nabla^2\Psi+\left(\frac{8mE}{h^2}\right)\Psi=0$

(c) $\nabla^2\Psi+\left(\frac{2mE^2}{h}\right)\Psi=0$ (d) $\nabla^2\Psi+\left(\frac{2m}{h^2}\right)\Psi=0$

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108. The Hamiltonian operator (Ĥ) is given by:

(a) $-\frac{\hbar^2}{2m}\nabla^2+V$ (b) $-\frac{h^2}{2m}\nabla^2+V$ (c) $\frac{\hbar^2}{2m}\nabla^2+V$ (d) $\frac{h^2}{2m}\nabla^2+V$

109. The energy eigenvalues of the rigid rotor is given by:

(a) $E_1=\frac{l(l+1)h^2}{8\pi I}$ (b) $E_1=\frac{l(l+1)h^2}{8\pi I^2}$ (c) $E_1=\frac{l(l+1)h}{8\pi^2 I}$ (d) none of these

110. The energy of an electron, present in the n[th] orbit is:

(a) $E_n\alpha\frac{1}{n}$ (b) $E_n\alpha n$ (c) $E_n\alpha\frac{1}{n^2}$ (d) $E_n\alpha n^2$

111. The velocity of an electron in the n[th] orbit of an atom is:

(a) $\upsilon_n\alpha\frac{1}{n}$ (b) $\upsilon_n\alpha n$ (c) $\upsilon_n\alpha\frac{1}{n^2}$ (d) $\upsilon_n\alpha n^2$

112. The radius of the n[th] orbit of an atom is:

(a) $r_n\alpha\frac{1}{n}$ (b) $r_n\alpha\frac{1}{n^2}$ (c) $r_n\alpha n^2$ (d) $r_n\alpha n$

113. The De- Broglie's equation is:

(a) $\lambda=\frac{h}{\sqrt{(2meV)}}$ (b) $h=\frac{\lambda}{\sqrt{(2meV)}}$ (c) $\lambda=\frac{h}{\sqrt{2m}}(eV)$ (d) $h=\frac{\lambda}{\sqrt{2m}}(eV)$

114. The first use of quantum theory to explain the structure of atom was made by:

(a) Bohr (b) Planck (c) Rutherford (d) Summerfield

115. Highly energetic electromagnetic radiation is:

(a) IR [illegible] (c) Visible [illegible] (d) none

116. Bohr model can explain:

(a) The spectrum of Hydrogen molecule

(b) the spectrum of Hydrogen atom only

(c) The solar spectrum

(d) The spectrum of an atom or ion containing one electron only

117. The wavelength of [illegible] line of an electronic transition is mostly related to:

(a) the nuclear charge of the atom

(b) the difference in [illegible] involved in the transition

(c) the number of electrons undergoing the transition

(d) All the above

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118. The least stable ion amongst the following:

(a) B^- (b) Be^- (c) Li^- (d) C^-

119. The no. of nodal planes in a Px orbital is:

(a) 1 (b) 3 (c) 0 (d) 2

120. In the most stable elements the no. of protons and neutrons is:

(a) odd- odd (b) even –even (c) even- odd (d) odd-even

121. The stability of nucleus depends upon the ration:

(a) n/p (b) e/n (c) e/p (d) n/e

122. Binding energy of $_2He^4$ is 28.57 meV Calculate its binding energy per nucleon is:

(a) 4.74 meV (b) 57.14 meV (c) 7.14 meV (d) 19.28 meV

123. Nuclear forces are:

(a) inter nuclear forces (b) paratomic forces

(c) electrostatic (d) exchange forces

124. Identify the correct order of boiling points of the following compounds:

1. $CH_3CH_2CH_2CH_2OH$
2. $CH_3CH_2CH_2CHO$
3. $CH_3CH_2CH_2COOH$

(a) 1 > 3 > 2 (b) 3 > 1 > 2

(c) 3 > 2 > 1 (d) 1 > 2 > 3

125. Specify the coordination geometry around the hybridization of N and B atoms in the 1:1 complex of BF_3 and NH_3

(a) N: pyramidal, sp^3, B: planar, sp^2

(b)N: tetrahedral, sp^3, B: tetrahedral, sp^3

(c)N: pyramidal, sp^3, B: pyramidal, sp^3

(d)N: pyramidal, sp^3, B: tetrahedral, sp^3

126. In the dichromate anion:

(a) 6 Cr – O bonds are equivalent (b) 4 Cr- O bonds are equivalent

(c) All Cr- O bonds are equivalent (d) All Cr – O bonds are non-equivalent

127. The correct order of hybridization of the central atom in the following species $[NH_3, PtCl_4]^{-2}$, PCl_5 is:

(a)dsp^3, sp^3, dsp^2 (b) sp^3, dsp^2, dsp^3

(c)dsp^2, dsp^3, sp^3 (d) dsp^3, sp^3, dsp^2

128. The hybridization of atomic orbital of nitrogen in NO_2^+, NO_3^- and NH_4^+ are:

(a) sp, sp^2, sp^3 (b) sp^2, sp^3, sp (c) sp^3, sp, sp^2 (d) sp^2, sp^3, sp^2

129. The geometry of H_2S and its dipole moment are:

(a) linear and non-zero (b) linear and zero

(c) angular and zero (d) angular and non-zero

130. The no. and type of bonds between two carbon atoms in CaC_2 are:

(a) one σ and one π bond (b) one σ and two π bonds

(c) one σ bond (d) one σ and one & a half π bonds

131. The hydrogen bond is strongest in:

(a) O - H .....S (b) F – H .....O

(c) F – H .....F (d) S – H .....O

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132. The Cl – C – Cl angle in 1, 1, 2, 2 tetrachloroethane and tetra chloromethane respectively will be about:

(a) 90^0 and 190.5^0 (b) 109.5^0 and 120^0

(c) 120^0 and 109.5^0 (d) 109.5^0 and 90^0

133. On hybridization of one s and one p orbital we get:

(a) two orbital at 180^0 (b) three orbital in a plane

(c) one mutually perpendicular orbital (d) four orbitals directed tetrahedrally

134. Which does not has hydrogen bonding?

(a) Liquid NH_3 (b) Phenol

(c) H_2O (d) liquid HCl

135. CCl_4 has no dipole moment because of:

(a) Tetrahedral structure (b) Planar structure

(c) Similar size of C and Cl atoms (d) Similar electronegativities of C and Cl

136. The formula of a compound is X_2Y_3. The no. of electrons in outer most shells of X and Y are:

(a) 5, 6 (b) 3, 2 (c) 2, 3 (d) 6, 2

137. A sp^3 hybrid orbital contains:

(a) ½ s character (b) ¼ s character

(c) 2/3 s character (d) ¾ s character

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Answers (Structure & Bonding)

1.a	2.d	3.b	4.a	5.c	6.d	7.a	8.b	9.c	10.a	11.b	12.b	13.c
14.c	15.a	16.d	17.a	18.c	19.c	20.a	21.a	22.a	23.a	24.a	25.d	26.b
27.c	28.c	29.b	30.a	31.c	32.a	33.a	34.a	35.c	36.c	37.a	38.c	39.a
40.d	41.b	42.a	43.a	44.b	45.a	46.c	47.a	48.c	49.a	50.a	51.c	52.c
53.c	54.b	55.c	56.c	57.b	58.d	59.a	60.c	61.b	62.d	63.c	64.b	65.b
66.a	67.b	68.a	69.c	70.b	71.d	72.a	73.c	74.c	75.c	76.d	77.a	78.b
79.a	80.b	81.b	82.a	83.a	84.c	85.c	86.a	87.c	88.a	89.b	90.b	91.d
92.a	93.a	94.b	95.a	96.c	97.c	98.c	99.b	100.b	101.a	102.d	103.a	104.b
105.c	106.b	107.d	108.a	109.a	110.c	111.a	112.d	113.a	114.a	115.b	116.d	117.b
118.b	119.a	120.b	121.a	122.c	123.d	124.b	125.b	126.a	127.b	128.a	129.d	130.b
131.c	132.c	133.a	134.d	135.a	136.a	137.d						

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